

8-20-2013

Selective Area Laser Deposition For The Purpose Of Ceramic Joining And Repair

Clayton M. Weiss

University of Connecticut, clayton.weiss@gmail.com

Follow this and additional works at: <https://opencommons.uconn.edu/dissertations>

Recommended Citation

Weiss, Clayton M., "Selective Area Laser Deposition For The Purpose Of Ceramic Joining And Repair" (2013). *Doctoral Dissertations*. 212.

<https://opencommons.uconn.edu/dissertations/212>

Selective Area Laser Deposition

For the Purpose of

Ceramic Joining and Repair

Clayton Michael Weiss, PhD

University of Connecticut, 2013

Ceramic materials present joining and repair difficulties that metallic and polymeric materials often lack. The high working temperature and potential for thermal decomposition make techniques such as welding and adhesive bonding unfeasible or impractical. It is possible to create ceramic materials from gas phase precursors through the use of chemical vapor deposition methods. A laser can create localized heat in a substrate and cause the productive decomposition where spatially desired. Through computer motion control, arbitrary patterns of ceramic deposits can be grown. This technique can be used to make free form objects. This process is known as selective area laser deposition (SALD). A similar process of selective area laser deposition and vapor infiltration (SALDVI) uses a powder bed to create more uniform depositions. Through the use of these techniques, while defining the negative space of a joint as the envelope for a three dimensional deposit, it is possible to form a joint fill. The process can be used to create a variety of ceramic compositions by manipulating the precursor gas combinations. The design of a deposition-joining system is presented. The system is operated as a proof of concept to create, silicon carbide, silicon nitride and aluminum oxide deposits and joints. These different systems are characterized to show the potential for this technology.

Selective Area Laser Deposition

For the Purpose of

Ceramic Joining and Repair

Clayton Michael Weiss

B.S., George Washington University, 2006

A Dissertation

Submitted in Partial Fulfillment of the

Requirements for the Degree of Doctor of Philosophy

at the University of Connecticut

2013

Copyright by
Clayton Michael Weiss

2013

Approval Page

Doctor of Philosophy Dissertation

Selective Area Laser Deposition For the Purpose of Ceramic Joining and Repair

Presented by

Clayton Michael Weiss, B.S.

Major Advisor_____

Harris L. Marcus

Associate Advisor_____

Mark Aindow

Associate Advisor_____

George A. Rossetti

University of Connecticut

2013

Acknowledgments

The work in this dissertation could not have been accomplished without the help and support of my advisor Harris Marcus. Dr. Marcus helped me become a good scientist while allowing me the freedom to make my own mistakes and my own discoveries. My advisory committee provided valuable insight that helped craft the course of my research. My research was possible through funding from the Connecticut Center for Advanced Technology, The GAANN Fellowship and the Institute of Materials Science. Many people in the IMS faculty and staff also helped me with my research. Finally my parents provided continued support and encouragement over the course of my research.

Table of Contents

Abstract	i
Title Page	ii
Copyright	iii
Approval Page	iv
Acknowledgments	v
Table of Contents	vi
Introduction	1
Selective Area Laser Deposition (SALD)	3
Selective Area Laser Deposition and Vapor Infiltration (SALDVI)	8
Precursor Selection and Evaluation	18
System Design	25
System Evaluation and Silicon Carbide Test Deposits	49
Silicon Carbide Joining	
Introduction	54
Experimental Procedure	55
Results and Discussion	59
Conclusion	71
Selective Area Laser Deposition for Silicon Nitride Joining	72
Chemistry Selection	73
Experimental Set Up	74
Experimental Results	76

Characterization	78
Conclusion	85
Aluminum Oxide Precursor Evaluation	86
Alumina Precursor Evaluation for SALD Joining	88
Selective Area Laser Deposition Joining of Aluminum Oxide	99
Introduction	100
Experimental Materials and Methods	104
Experimental Results	107
Conclusion	117
Future Modifications to Enhance Process	118
Conclusions	120
References	122

Introduction

The joining of ceramic materials is an important step in ceramic manufacturing. The high temperature materials often have high melting temperatures or decompose at elevated temperatures. Welding is not a viable type of joining for ceramic materials as it is for metals. In order to join ceramics a variety of joining techniques are used including: brazing, mechanical interlocking, adhesive joining, microwave or friction welding or high temperature- high pressure sintering. [1] [2] [4] [29] There are numerous techniques for working with ceramics in the green state including joining of components before firing. [7] Once a part is formed it becomes a challenge to join it to another ceramic part. For certain applications joining in the green state is not an option and the green state joining is not useful for repairs. The other joining techniques either introduce a separate low temperature phase such as adhesive joining and brazing, or necessitate that the part be subjected to high temperatures and pressures, which could be damaging to the work piece. It is often undesirable have a joint fill of a different composition than the parent

ceramic due to potential thermal expansion mismatch. The introductions of a lower temperature braze limits the system working temperature to the working temperature of the brazing compound. Additionally, some environments, such as high radiation areas, may be unsuited to the presence of metal. [12] An ideal ceramic joint would join two ceramic work pieces with a joint fill material that is the same chemical composition. The resulting joint should be monolithic and display the same properties as the individual work pieces while also forming a chemical bonds with the two joint substrates. In order to make such a joint it is necessary to locally deposit ceramic material. There are joining techniques that create a ceramic filler in-situ, such as transient liquid phase bonding and reaction bonding, [12][42] but these techniques involve subjecting a part to high temperature. In order to deposit a material without subjecting the piece to damagingly high temperatures it is necessary to use a process that converts precursor chemicals to ceramics in situ without subjecting the work piece to extreme conditions.

Pyrolytic chemical vapor deposition is a fabrication technique that converts precursor gasses to solid coatings through a process of thermal decomposition. A work piece is brought to an elevated temperature and exposed to a gas or combination of gasses that contain the chemical species' required, to form, the desired deposit material. While this technique is widely used and highly effective at creating uniform coatings of a desired thickness, the entire work piece becomes coated unless some type of mask is employed. Most pyrolytic chemical vapor deposition (CVD) reactions can be categorized as either hot wall or cold wall reactions. In both cases the substrate is brought to the thermal decomposition temperature of the precursor gas resulting in a coating type deposition on

the substrate. In a hot wall reaction the reaction chamber is heated to the decomposition temperature and both the chamber and the substrate become coated with the deposited material. In a cold wall reaction only the substrate is heated. [40] In both of these cases, a uniform coating process occurs and is usually the objective. Uniform coatings do not lend themselves to the formation of good joints or the formation of three-dimensional objects. The formation of joint through chemical vapor deposition would require that the joint fill area alone be heated resulting in localized deposition and growth. In order to create a localized deposition, the technique of laser chemical vapor deposition can be used. LCVD uses a laser as the driving force for the conversion of precursor gas to a desired product. The reaction can be either photolytic, or pyrolytic, with the laser either providing a triggering wavelength or an elevated temperature zone, respectively. [32] Of interest in this study is the pyrolytic decomposition of precursors. In LCVD a laser is used to impart a high energy per unit area to a substrate surface. This high input of energy can rapidly heat the surface to decomposition temperature while minimally penetrating the substrate. [3] While a laser is used to impart energy to a surface, LCVD is still used primarily in a surface coating mode. A specialized use of the LCVD process adds spatial selectivity and the ability to scan the laser beam, creating bulk three-dimensional deposits as apposed to coatings.

Selective Area Laser Deposition (SALD)

Selective area laser deposition (SALD) is localized chemical vapor deposition technique. SALD is a process that uses a volatile liquid or gaseous chemical precursor that contains

the chemical species needed to produce a solid deposition through the action of pyrolytic decomposition. The precursor or precursors used can be used to create both metals and ceramic surface deposits; however, the use of pre-ceramic precursors is of the most practical interest. [3] By tailoring the chemical composition of the precursor gasses it is theoretically possible to get a wide range of deposited chemistries. [57][58] The chemistries of interest are those of high strength, high temperature technical ceramics.

The SALD process begins with the introduction of process gasses into a vacuum reaction chamber. The gases are introduced in ratios that will promote the growth of the desired ceramic upon decomposition. A deposition substrate is within the vacuum chamber and will be used for ceramic growth. Through the use of computer controlled optical positioning, a laser is scanned onto the deposition surface. The laser used must couple with the substrate, and the deposited material that subsequently becomes the substrate, and heat the surface to a desired temperature. The temperature is sufficient to cause the thermal break down, or pyrolysis, of the process gasses in the chamber. The gasses that are heated near to, and ideally, those adsorbed on to the substrate surface, thermally decompose. A ceramic product is left on the substrate and gaseous reaction products diffuse away from the surface.

As the laser is scanned across the substrate surface, in an arbitrary pattern, a line of ceramic material is deposited. The deposited material line is approximately the size of the laser spot. By rastering the laser across a surface in a specific pattern a filled shape can be formed. Through repeated passes it is possible to make a deposited layer of

ceramic in a specific shape. By depositing subsequent layers of ceramic material three-dimensional shapes can be formed. The process is a type of additive manufacturing that is capable of making three-dimensional objects. [3][10][24][57]

The SALD process is a chemical vapor deposition process (CVD). CVD processes are used to make surface coatings of ceramic materials. The CVD processes are indiscriminate in the application of heat to the substrate surface. With uniform heating there is uniform growth across the surface in the ideal system. There exists a class of CVD that uses laser beams to heat the substrate surface, Laser Chemical Vapor Deposition (LCVD). SALD is a laser driven process similar to LCVD but more specialized. The laser can create a localized hot spot, through focusing, that has enough irradiance (W/M^2) to initialize the thermal decomposition of the precursors. SALD uses the laser spot as a decomposition area limiter as apposed to LCVD, which is using the laser just to achieve an energy density on the substrate surface. [3][32][35]

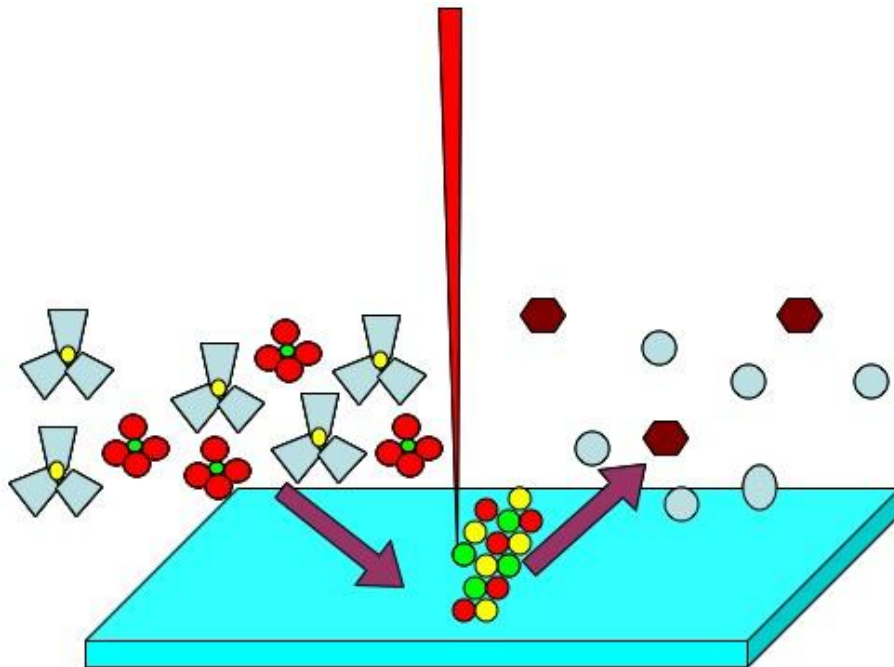


Figure: 1

Schematic representation of the SALD process is shown. Gas phase precursors diffuse to the substrate surface. Scanning the laser across the substrate, selectively heats it, forming deposits of ceramic material. Gas phase reaction products diffuse away from the surface and mix with the gas environment.

Laser spot size and laser power (for CW lasers) can be manipulated to affect the laser irradiance. The irradiance I , quantifies, power of electromagnetic radiation per unit area (W/M^2). Irradiance, and the degree to which the laser light is absorbed into the substrate, both influence the laser spot temperature. The spot temperature dictates whether or not there will be decomposition and at what rate this decomposition occurs. In short the hotter the spot temperature the faster the reactant gasses will be converted to decomposition products as long as there is available precursor at the reaction site. There

are limits; however, on how hot the substrate can be. Substrate ablation and undesired decomposition products can result with spot temperatures that are too high. [32] The laser I can be found by taking the average laser power and dividing this figure by the spot size at the substrate surface. For example: if a laser is operated at 10 W, and has a beam diameter of 100 microns, the Irradiance at the substrate is 1.3 (GW)/M^2 . Focusing the laser has a very large effect on the laser irradiance. The laser spot temperature needs to be quite high in order to correctly decompose the precursors; temperatures of the order of 1000 C are common. [58] [49]

To deposit ceramic materials, using the SALD system, appropriate precursors must be selected. The chemical reactions that are used in SALD are gas phase reactions that happen on the surface of a solid substrate. The selection of a gas phase precursor is important to the deposition process. Ceramics such as silicon carbide (SiC), silicon nitride (Si_3N_4), and aluminum oxide (Al_2O_3), illustrate the diversity and levels of complexity of the precursors necessary. Ideally a single source precursor would be used; a gas that will decompose directly to the desired ceramic. Silicon carbide is an example of a material made from a single major precursor, though additional process gasses are added. Tetramethylsilane $\text{Si}(\text{CH}_3)_4$ contains both silicon (Si) and carbon (C), which are both available to form SiC. Silicon nitride represents the next level in precursor complexity. A source of Si and a source of N are needed to form this compound. There is not a gas precursor that contains both of these elements so it is necessary to use multiple major precursors. Forming an oxide such as aluminum oxide again suggests another level of complexity, as the addition of an oxide precursor must be controlled to

prevent a gas phase reaction. Metal-organic gasses can present additional challenges as they can be pyrophoric or highly reactive.

Selective Area Laser Deposition and Vapor Infiltration (SALDVI)

Selective area laser deposition and vapor infiltration (SALDVI) is a variation of the SALD technique. SALD is the deposition onto a substrate where each deposited layer becomes the substrate for the next deposited layer in a form of additive manufacturing. SALDVI uses a powder bed as the substrate. The deposit forms within the powder bed; each powder particle becomes a three dimensional substrate for ceramic growth. As the precursor gasses infiltrate the powder bed the particles are heated by the incoming laser radiation. The particles are heated to the decomposition temperature and growth occurs on all sides of the particle. The coating on adjacent particles grows and ideally the deposit fills the interstitial space. [8][10][13][20]

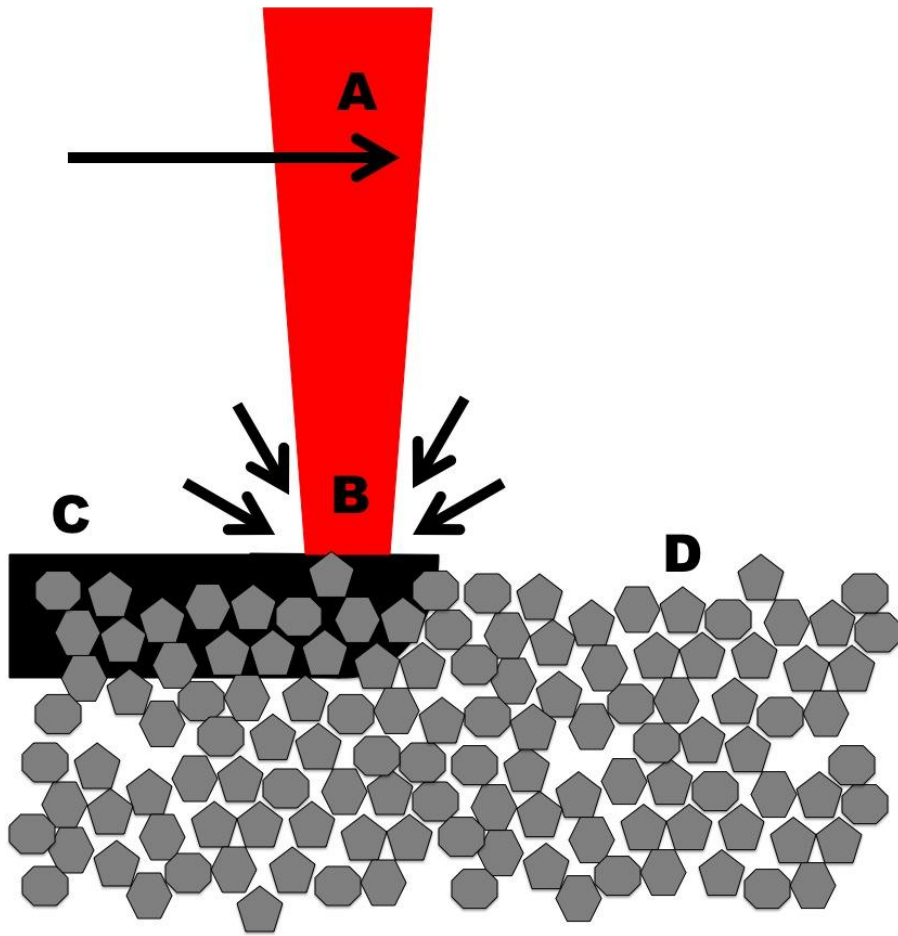


Figure: 2

Schematic depiction of SALDVI is shown. The laser A is scanned in the direction indicated by the arrow. The area of beam incidence B, is heated to the decomposition temperature. Process gas diffuses to this point and infiltrates the powder bed, D. The infiltrated gasses have been converted to a solid deposit binding the substrate powder in area C.

SALDVI has both advantages and disadvantages with respect to the SALD process.

SALD deposits have the potential to be completely filled whereas the SALDVI deposits can retain voids after deposition. Since the reaction gasses must diffuse into the spaces between the particles, before decomposition, decomposition can be halted if this pathway is cut off. Voids between powder particles can become trapped within the deposit. If the powder packing density is too high the necessary diffusion becomes difficult and incomplete deposits can result. [13]

SALDVI does present advantages over the SALD process. The SALD process is a relatively slow process; gasses must diffuse to the substrate and decompose there. Growth times of several days are not uncommon. Only small volumes of gas react with the hot zone and decompose at any time. The SALDVI process can decrease the work piece build time. A substantial part of the volume of the final, solid freeform, structure is made up of powder that existed preceding the deposition. The SALD process deposition rate can be fundamentally increased because of this volume saving mechanism. [8] The SALDVI process can also result in more uniform deposits. A particle can be more readily heated to the deposition temperature than a solid substrate. Heat loss, by conduction, is limited in a small particle as the contact surfaces with adjacent particles are primarily point contacts. Most of the surface of a particle is surrounded by gas with a lower thermal conductivity than the substrate material. Heat transfer by convection is also limited within a powder bed compared to the convective transfer at the free surface. [32] Particles in the SALDVI process can absorb the laser radiation readily and keep the heated area more localized than the SALD process, this results in a more uniform growth.

The SALDVI process is more controllable than the SALD process. Runaway heating is not uncommon during the SALD depositions. If a given area, such as a small protuberance, becomes super heated during the SALD process a runaway growth can result. The higher the temperature, above the decomposition temperature, the more rapidly the decomposition reaction takes place. [40]

The chemical composition of the powder used in a SALDVI deposit can be the same or different from the composition of the deposited ceramic. If the deposited material and the powder substrate are the same chemical composition the final structure is chemically homogeneous. If a powder that is dissimilar from the deposited material is used, the deposition process makes a composite structure. The powder serves as a reinforcement phase while the chemical vapor deposit serves as a matrix. This composite effect increases the versatility of the SALDVI process. It is possible to make metal-ceramic composite materials with this technique. [13]

The SALD and SALDVI processes have several technical applications. Since the computer positioning system and the X-Y positioning stage, control the depositions, intricate deposits are possible. By programming a laser path it is possible to create arbitrary in plane designs that can be layered on each other. In this fashion three-dimensional objects can be fabricated. As with many additive-manufacturing techniques the process gives great flexibility of design. Since the deposition processes are making ceramic materials, these intricate and arbitrary shapes can be formed out of, normally, difficult to work materials. Ceramic materials are known for their high hardness and heat

resistance. These qualities make them difficult to machine and in many cases impossible to melt. The SALD and SALDVI processes circumvent these limitations by directly depositing the ceramic materials. The precursor decomposition temperatures are lower than the ceramic decomposition or melting temperatures, which means that work pieces are not damaged by excessive heat. Furthermore, since the processes are localized there is limited bulk work piece heating. It is this property as well as the high degree of spatial selectivity that allows the deposition processes to be used for ceramic joining or repair.

The use of SALD and SALDVI techniques can provide the means of locally depositing ceramics for the purpose of joining other ceramics. The high degree of spatial deposition control and the flexible nature of the programming allow the formation of ceramic-ceramic joints. The process can use a variety of precursors so ceramic joints can be formed with several classes of ceramic material; carbide, nitride and oxide ceramic joint fills are explored in this study.

Selective area laser deposition and selective area laser deposition and vapor infiltration experiments have been previously performed with several objectives. Silicon carbide as a decomposition product was chosen in early SALD studies. A single source precursor of Tetramethylsilane (CH_3)₄Si has been used as the source of both carbon and silicon. Initial SALD studies showed that chemical vapor deposition systems designed to deposit silicon carbide could be modified for use with the SALD process.[21] [24] [34][35][58]

Part of the versatility of the SALD process is the potential for wide variety of precursors resulting in a wide range of deposited material. Previous studies of different conventional CVD systems yielded an array of potential SALD precursors. [49][58] If the precursors, were already gas or had a high vapor pressure at room temperature, and showed a chemical stability at room temperature, while productively decomposing at an elevated temperature, they were suitable candidates for SALD precursors. [20][21][24] Several systems were explored in practice.

Though the SALD process gasses are introduced as batch reaction, as apposed to a continually flowing system, it is possible to make structures that are composed of multiple material systems. Each layer of deposited material can be of a different composition by flushing out the process gasses and modifying the successive gas composition. In this way it is possible to make functionally structures with a varied internal chemistry. A proof of concept thermocouple device was created with a combination of SALD and SALDVI deposits of silicon carbide, silicon nitride and vapor deposited carbon. A SiC/C thermocouple junction was formed encased within Si_3N_4 insulation. [10]

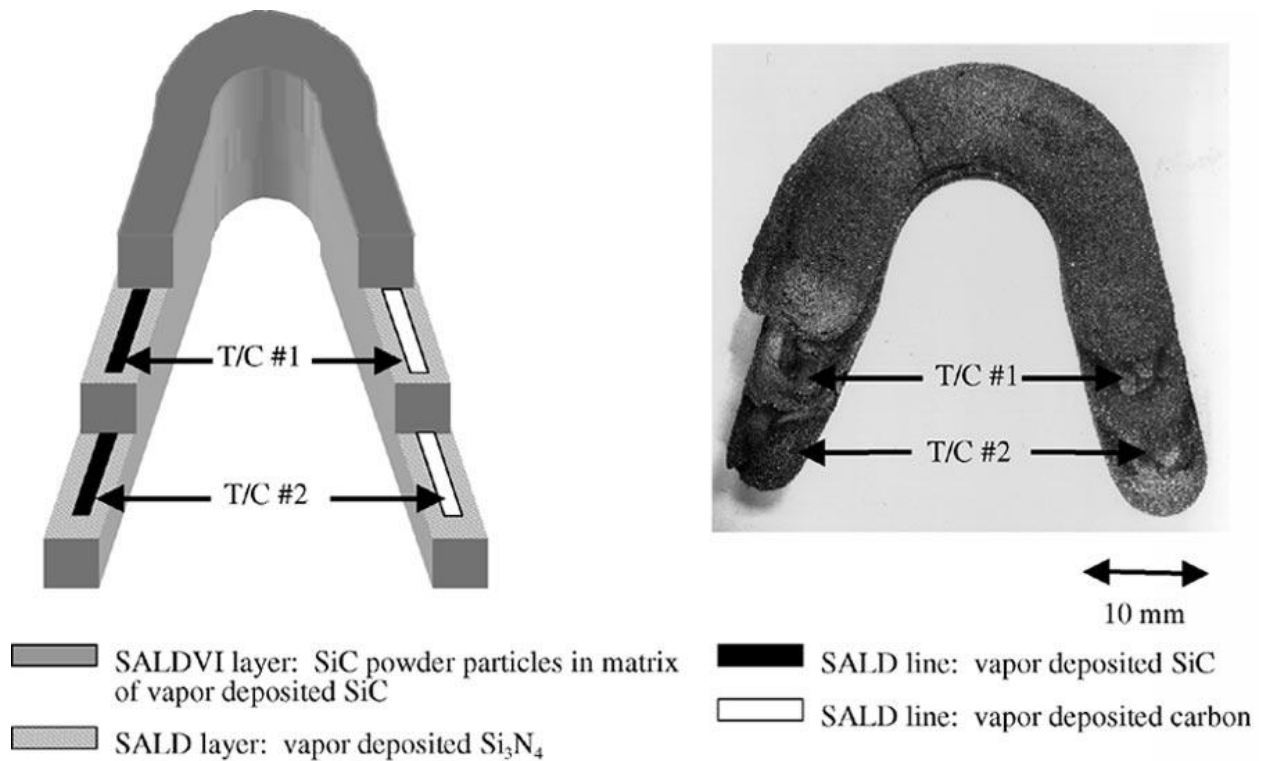


Figure: 3

Work of James Crocker et. al., showing an in situ thermocouple of SiC and C deposited by the SALD deposition process, is shown. The experiment showed the potential for forming in situ devices and the versatility of the SALDVI and SALD processes.

Joining attempts have been performed using the SALD process. Spot joining of silicon carbide and silicon nitride were attempted where samples were clamped together and exposed to a stationary laser spot in the precursor gas environment. With the stationary deposit it was possible to join SiC and in some cases Si₃N₄ though with limited success in the latter case. [17] A customized joining system was created with the purpose of joining

silicon carbide tubes of a predetermined geometry with a SALD deposit. The joining of SiC tubes with silicon carbide filler was performed in a system that utilized a set of computer controlled goniometer mounted mirrors to direct a laser beam at the junction of two ceramic tubes. The laser was oscillated while the tube was rotated resulting in a circumferential deposit. The joint quality of these deposits was good though the joining technique is limited in scope due to the highly specific work piece requirements. [20]

[21] Shown below are three examples of previous joining experiments:

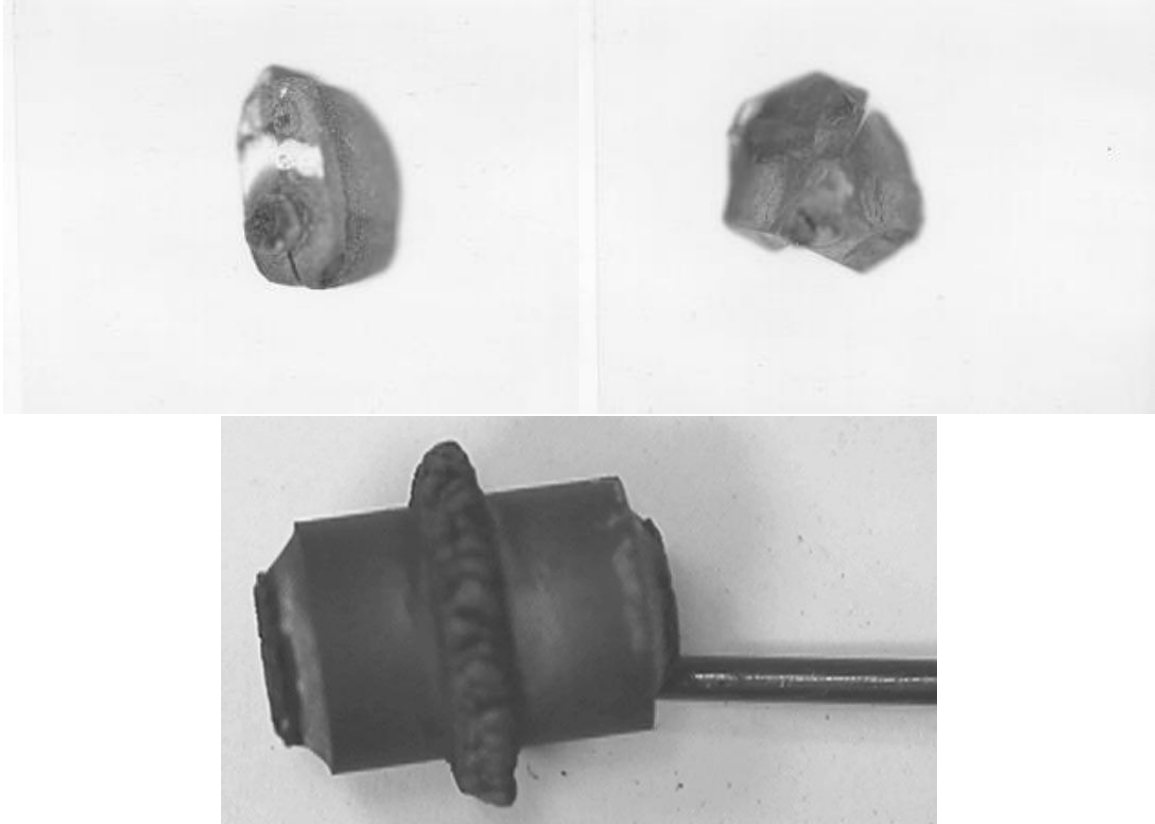


Figure: 4

Previous work concerning SALD joining is shown. Spot joining of SiC/SiC (A) and Si₃N₄ (B) are shown. SALD deposit of SiC forming a circumferential tube joint is indicated (C). [17][20][21]

SALDVI work has focused primarily on the creation of solid free form objects. SiC objects created by infiltrating a variety of powder compositions have been explored. The SALDVI process borrows technologies developed for selective laser sintering (SLS) to achieve even powder distribution of a controlled thickness. [9] SALDVI experimental series concerned the infiltration of TMS into various powder beds and subsequent decomposition. A variety of powder distribution systems were tested. Experiments

focused on the rate at which the precursor is absorbed into the powder bed and the relationship between this absorption and the deposited layer thickness and the interlayer bonding. [13] The laser-powder interaction was also evaluated. The density of the final products and degree of stratification were evaluated and work was done to optimize the silicon carbide deposit uniformity. SALDVI of silicon carbide deposited into silicon carbide powder and other powders have been extensively characterized. [13]

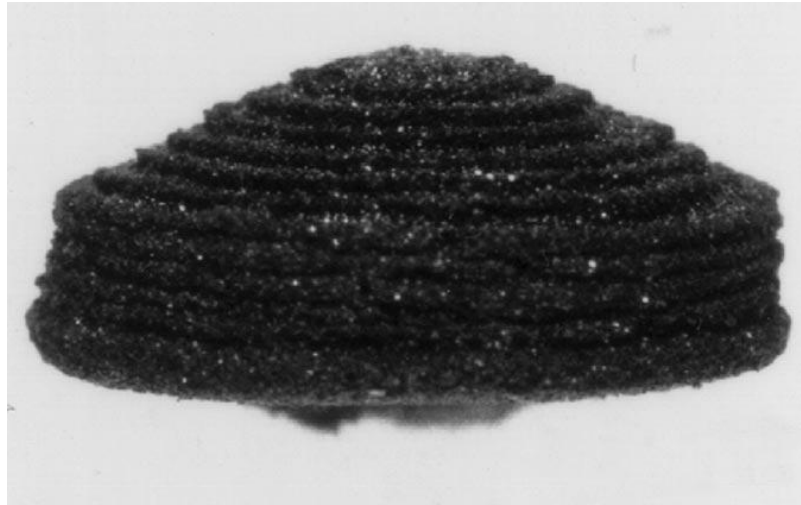


Figure: 5

An arbitrary three-dimensional shape deposited by SALDVI is shown. This is a SiC structure that was made through the infiltration of SiC powder with TMS.

[10]

Precursor Selection and Evaluation

An essential step in the SALD process is the selection of precursor chemicals. The precursor chemicals are used as the source of elements that make up the desired ceramic material. In order to be considered as a precursor for the SALD chemical vapor deposition process, the compound must exhibit several specific attributes. The precursor must be in a gaseous state at the temperature and pressure conditions used for the deposition. In order to be so, a precursor can be a gas at standard temperature and

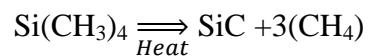
pressure or must be capable of forming a gas at a decreased pressure. Gasses such as ammonia NH_3 , carbon dioxide CO_2 , acetylene, C_2H_2 , and methane CH_4 are molecular compounds that can be used as chemical sources in the SALD process. Elemental gasses such as N_2 , H_2 , and O_2 can also be used as precursor gasses. [40]

It is possible to use a compound that is a liquid at STP provided that this liquid can be vaporized and remain in the gas phase for the duration of the experiment. In order for this to be the case the compound must have a sufficient equilibrium vapor pressure at the temperature of the reaction chamber. While certain chemical vapor deposition reactions utilize low partial pressures of reactive gasses, (< 1 torr), these reactions produce very small volumes of deposited material making build times prohibitively long. SALD reactions require that much greater volumes of deposited material be produced in a localized area. Deposition volume is of the order of cubic mm. A higher vapor pressure allows increased reaction rates and greater volume of deposit per volume of reaction chamber. [24][32][40] For SALD reactions it is preferable to have precursors with equilibrium vapor pressures in the range of the tens to hundreds of torr. [32] A lower limit is not fixed but equilibrium vapor pressures >5 torr will greatly facilitate the growth of SALD deposits on the macro scale.

The gas phase precursor must be stable and unreactive when introduced to the reaction chamber. In order to be useful for the SALD process the precursor must remain stable at lower temperatures and decompose cleanly at an elevated temperature. If the gas is

unstable at the chamber operating temperature, the precursor will decompose without the use of the laser thermal source and consequently will deposit in a non-localized manner.

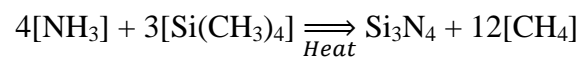
The stability of the precursor and its unreactivity at operation temperatures, are required characteristics but the function of the precursor is to provide the elemental building blocks needed for the deposition process. A single source precursor would provide the elemental composition needed to make the correct composition of the deposit. Silicon carbide (SiC) has been made through the thermal decomposition of tetramethylsilane (TMS). The chemical reaction relevant to this process is shown below:



Tetramethylsilane decomposes by a high temperature (≈ 1000 C). The decomposition products are, the desired silicon carbide, and a waste gas (methane). TMS exhibits the characteristics of a well-selected precursor for the SALD process. TMS has a high equilibrium vapor pressure, 603 torr at 20 C [44], and is stable at this temperature. The composition of the precursor gas contains the elements required for the formation of SiC in the correct stoichiometric ratios. The gas phase reactant yields a solid and a gaseous product, the solid is the desired ceramic and the gas diffuses away from the reaction zone.

TMS is a single source precursor, which yields silicon carbide on pyrolytic decomposition. In order to make silicon nitride it is necessary to combine the source of

Si, (TMS) with a nitrogen source. It has been shown that the addition of ammonia (NH₃) to the TMS in the correct ratios can be used as a nitrogen source. [17][49][56] Ammonia is also a good example of a SALD precursor. Anhydrous ammonia can exist as a vapor at atmospheric pressure. Ammonia is a gas at room temperature and atmospheric pressure. Since SALD depositions occur in a vacuum chamber and are always performed in a partial vacuum, this vapor pressure is more than adequate. Ammonia is also stable at room temperature and does not react in the gas phase with TMS.



The decomposition reaction of TMS and NH₃ is shown. The decomposition yields solid silicon nitride and gaseous methane. In practice, TMS for SiC and TMS and NH₃ for Si₃N₄ are used in conjunction with other process gasses. Hydrogen and an inert gas are added to the reactant environment. One of the problems with SALD process is the creation of unwanted hydrocarbon contamination. A large fraction of the reaction gasses contain hydrogen and carbon. Ideally these extra components will be converted to minimally reactive methane; however, partial decomposition of the reactant gasses can occur. [40] Hydrogen is added to the reaction to reduce this contamination and promote the more complete conversion of the reactants. [43] [14]. The addition of an inert gas such as helium or argon assists in the formation of a laser plasma. [3] The ionized zone formed by the laser serves to reduce the hydrogen availability in the deposited material[Laser-assisted plasma-enhanced chemical vapor deposition of silicon nitride thin film]. The reduced hydrogen incorporated into the deposit results in a lower level of

deposit contamination. The energetic plasma created by the beam is present in all SALD decomposition reactions.

The addition of the inert gas also serves to raise the system total pressure. The pressure in the system is related with the total amount of gas available for convective heat transfer. A hot zone is a necessary component of the SALD process. The substrate has to reach the decomposition temperature, but if the gaseous environment reaches this temperature, gas phase decomposition can result. The gas concentration can be used to affect the local temperature outside of the direct beam but the addition of reactive gasses is not always feasible.

The precursor selection process for aluminum oxide is has additional complexity compared to SiC and Si₃N₄. It is necessary to find a precursor with a source of aluminum that can exist in the vapor phase as well as a separate oxygen component. From the literature it is shown that aluminum oxide is made through several different chemical vapor deposition routes. Aluminum oxide is an example of a material that has several suitable precursors for conventional CVD that are unsuitable for the SALD process.

Several Al₂O₃ precursors are solid at room temperature. Solid precursors either have very low vapor pressures or must be converted into a more volatile form. The conversion to a more volatile state is done primarily through the use of elevated temperatures or the presence of solvents. [47][54] Aluminum chloride (AlCl₃) vapor can be used as the aluminum source for chemical vapor deposition but aluminum chloride is a solid at room temperature and must be heated to >100 C to create a vapor. AlCl₃ at 100 C has a vapor

pressure of 1 torr, the material sublimes at 190 C, [37][45] the vapor is then toxic and corrosive. It is also necessary to keep the reaction chamber at a high temperature in order to keep the vapor from condensing on the chamber wall. [40] The SALD process is usually operated as a cold wall process with the heat zone only occurring where the laser impinges, though system modifications were made to allow for heating. Heating the reaction chamber, to an intermediate temperature (<300 C), is possible but aluminum chloride was not used because of general incompatibility of solid-state precursors with the SALD process.

Other aluminum bearing solid state precursors include aluminum acetylacetonate, also known as aluminum 2,4-pentanedionate ($\text{Al}(\text{C}_5\text{H}_7\text{O}_2)_3$), $\text{Al}(\text{acac})_3$ [46]. On a first evaluation this seems like a good precursor as it contains both aluminum and oxygen that would be available for the decomposition process and a single source precursor simplifies the SALD process. The $\text{Al}(\text{acac})_3$ is a solid at room temperature with a melting point of 190 C and a boiling point of 315 C [45]. The operating temperature would be too high for the SALD system and the powdered precursors even in a vapor form require special delivery apparatus and are most efficiently delivered by carrier gas. Solids that have been vaporized are best delivered with a gas bubbler system, with a heated gas that is then driven through a flowing system. This would require extensive modifications to the SALD system. There are several more solid aluminum sources, aluminum hexafluoroacetylacetonate, aluminum 2,2,6,6-tetramethyl-3,5-heptanedionate, aluminum isopropoxide ($\text{Al}(\text{O}-i\text{C}_3\text{H}_7)_3$), aluminum tert-butoxide ($\text{Al}(\text{O}t\text{C}_4\text{H}_9)_3$),

that all have the same disadvantages for the SALD process. All of these compounds must be heated to >100 C in order to get a usable vapor pressure. [45]

The precursors best suited for the SALD process, if not already gasses, are volatile liquids. In this category are the compounds Trimethylaluminum, $\text{Al}(\text{CH}_3)_3$ (TMA), and Aluminum borohydride ($\text{Al}(\text{BH}_4)_3$). Aluminum alkyls, of the form AlR_3 where R is an organic radical, such as methyl, ethyl, etc., are often suitable aluminum sources for chemical vapor deposition. [25] These precursors do have a disadvantage of being dangerous and difficult to work with and potentially pyrophoric. Several sources have indicated that TMA is regularly used to form Al_2O_3 in CVD processes. [6][26][48][54] Small quantities of oxygen introduced into the reaction system will cause the conversion of TMA to Al_2O_3 [18][19], larger amounts cause an uncontrolled gas phase decomposition reaction. This indicates that the absorption of TMA onto a surface is self-limiting. This also indicates that several sources of oxygen will spontaneously react with TMA, which is undesirable in the SALD process. Spontaneous conversion in the CVD mode is not acceptable for SALD so a different source of oxygen is necessary. TMA has been explored as a precursor suitable for atomic layer deposition, where the TMA and oxidizer gasses are cycled into the reaction chamber and self-arresting layers are formed. [18][19] This indicates that the absorption of TMA onto a surface is self-limiting. This also indicates that several sources of oxygen will spontaneously react with TMA, which is undesirable in the SALD process. While this process is different than the SALD process, potential oxygen sources were indicated. H_2O , H_2O_2 , N_2O , and CO_2 have all

been used as oxidizers for the conversion to alumina with varied rates of reaction.

[6][18][19][26]

TMA is extremely reactive when combined with water vapor, hydrogen peroxide, or oxygen gas and will react in the gas phase without surface adsorption. In order to use the TMA as a SALD precursor it is necessary to have a source of oxygen that will not react in the gas phase with TMA. Organic compounds that contain oxygen within their structure such as diethyl ether, and methyl tert-butyl ether, are often highly volatile and have been used as oxygen sources for CVD. [11][22] There is evidence that ethers can form gas phase complexes. [Hydrogen Bonding in the Gas Phase: The Thermodynamic Properties of Hydrogen Fluoride-Ether Complexes and their Far Infrared Spectra]. Gas phase complexes of metal organic and oxygen bearing organic molecules could provide both metal and oxygen species. TMA is used in conjunction with diethyl ether as source of aluminum and oxygen as a gas phase complex.

System Design

The development of SALD and SALDVI techniques relies on the design and fabrication of certain experimental equipment. Deposition and joining applications define the characteristics and features necessary in this equipment. The SALD deposition reaction system can be described as a localized laser chemical vapor deposition system. Process gasses must be introduced into a reaction chamber. A reaction chamber contains the reaction gasses. A computer-controlled laser is directed and spatially positioned through

a viewport window to the reaction substrate. The laser can be modulated in power and positioned by a computer control system. An X-Y stage is used to position the laser optics through computer controlled servomotors. The reaction is monitored and controlled to produce the desired deposition conditions.

Since the deposition experiments operate in a partial vacuum, a vacuum capable chamber is necessary. Various steps in the deposition experiments require that the chamber also be capable of containing a positive pressure. All components used in the system were capable of being pressurized to a minimum pressure differential of 2 atmospheres. Several of the chemicals used in the SALD, and SALDVI processes require special containment and handling. Corrosive, oxidizing, flammable, and pyrophoric chemicals are introduced into the system for a variety of experiments. Stainless steel was used for all metal components. Metal on metal seals were used where possible for their resistance to chemical attack and their pressure containing capacities. The highest level of vacuum sealing utilizes deformable metal seals. [27] For larger seals, CF flanges were used and. Normally an annealed copper gasket would form the vacuum seal between the stainless steel knife-edges. Ammonia, used in the deposition of Silicon Nitride, is corrosive to copper and brass and can form explosive compounds with silver. [44] Considering this, silver plated or copper gaskets could not be used in all cases. For these conditions, the CF flange seals were replaced with aluminum gaskets. Smaller vacuum seals were made by VCR flanges, with nickel gaskets, Swagelok fittings, and NPT tapered fittings. The national pipe thread fittings achieve vacuum tightness through the use of Teflon tape. Component assembly was done with a combination of vacuum TIG welding and brazed

threaded connections. The Materials that directly contacted the reaction environment are, Stainless steel, Borosilicate glass, Teflon, and at different times, Copper, Nickel and Silver. Glass to metal seals were factory applied Kovar.

The deposition processes have several experimental stages. Liquid or gaseous precursors are contained in gas cylinders and must be introduced in a controlled fashion through a gas inlet manifold. The deposition chamber must contain enough reaction gas to produce a non-negligible amount of deposited material, so must be an adequate volume. A vacuum window provides the ingress point for the laser while being mechanically sound enough to withstand the differential pressure. Additional ports on the chamber are used to vacuum out atmospheric and process gasses and to evacuate the gas manifold.

Vacuum evacuation of the system, is controlled by a valve-controlled vacuum pump. Since the majority of experiments performed are in the 1-760 torr vacuum range and not at high vacuum, a mechanical rotary pump alone was chosen. An additional port that allows the venting of process gas is also necessary. The vent port is used in conjunction with a neutralization trap, to process the waste gasses. A gas manifold was designed to admit several gasses to the chamber.

A laser is used as a means of creating a hot spot for the purpose of thermal decomposition of the precursor gasses. The laser should be a single mode, TEM 00. [32] The laser power must be variable and controllable by an external computer. The wavelength of the laser must be suitable for the SALD process. For a wavelength to be suitable it must be absorbable by the substrate, and conversely must not be too readily reflected. [32] The

substrate must be capable of being heated to the point of precursor thermal decomposition. If there is too much reflection off of the substrate it is difficult to establish a decomposition zone. Infrared lasers are a good choice for several reasons. An infrared laser will couple with and absorb into many common materials to be used for the SALD process including many metals and ceramics. Short wavelength lasers, which can be highly energetic, can interact with the process gasses without the intermediate heating of the substrate. This can lead to gas phase decomposition and precipitation and not targeted growth. [3]

CO₂ and YAG, yttria aluminum garnet, lasers are both in the infrared range. CO₂ lasers have a primary wavelength of 10.6 microns. YAG lasers have a wavelength of 1064 nm. Both lasers are used as industrial lasers, which can heat metals and ceramics, often for the purpose of melting or cutting them. Beyond a choice of wavelength there is the choice of continuous wave, (CW) or pulsed lasers. A CW laser is a steady state system that is described in terms of power (W). A pulsed laser, characterized by J per pulse, releases its energy in discrete packets. [32] While the latter is useful when using the laser to cut, drill or otherwise ablate a surface, it can be too energetic for the decomposition substrate; concurrent deposition and ablation can be dominated by ablation.

The laser used in the first SALD experiments, of this experimental series, is a CW CO₂ laser with a nominal power of 50 W produced by Coherent. Laser power metering indicated that the true power was half of the nominal, as one of the lasing tubes was damaged. CO₂ lasers can be challenging to use because special optics are necessary.

Zinc Selenide, ZnSe optics must be used in CO₂ laser systems as materials that are optically transparent, such as glass, quartz, and sapphire, are opaque to 10.6- μ m-wavelength radiation. In order to direct the laser from its point of generation to the reaction site, ZnSe mirrors, lenses, and windows are necessary. External cooling water is needed to operate the CO₂ laser, increasing the operational complexity. The minimum focus possible with a CO₂ laser is greater than that of YAG by an order of magnitude due to the wavelength limitations.

A subsequent series of experiments were performed with a pulsed YAG fiber laser. Fiber lasers, are more modern and streamlined systems. The lasing media, resonating mirrors and fiber delivery systems all can be incorporated into the same fiber optic cable. Often a visible aiming laser can be incorporated into the fiber as well. Aiming lasers greatly facilitate laser alignment, which is an important and potentially dangerous part of working with any laser. Traditional lasers that are not fiber generated have external aiming lasers that can become misaligned with the primary laser beam. Both CO₂ lasers and YAG lasers generate beams in the infrared so are invisible to the human eye. YAG lasers have the added danger of being focusable by the lens of the eye, while the cornea absorbs CO₂ laser radiation. The pulsed laser used in these experiments, 1.5 mJ SPI, has a coaxially mounted beam collimator. Collimators are necessary for fiber lasers because the beam generated within the fiber will immediately scatter if the fiber diameter is smaller than the wavelength of the radiation. [23] A collimated laser beam is necessary for delivery through an optical train.

In addition to a pulsed YAG laser, a yttrium doped CW laser was also used. The laser is an IPG photonics laser with a hundred Watts of power and is also fiber generated, terminating in a collimator. The collimators used in these experiments produce a beam that is 3-5 mm in diameter. In order to use the laser for SALD experiments, it must be either exceedingly powerful or focused. The lasers used were focused using a focusing lens. The lens is situated outside of the reaction chamber so needs to have a long enough focal distance to pass through the window and reach the sample fixture.

The laser beam coming out of the laser body for the CO₂ laser, or the collimator for the YAG type laser is directed to the sample. This is done by a series of reflecting mirrors that are coated with wavelength specific reflective coatings. While these mirrors can reflect other wavelengths to some extent, they do not reflect as broad a spectrum as silvered mirrors do for visible light. It is beneficial to have the mirrors coated with dual reflective coatings, one for the primary beam and a coating for the aiming beam, in this case red. The laser is fixed with the outgoing beam parallel to the floor. A series of 45-degree mirrors, mounted on an X-Y positioning table, are capable of redirecting the beam from a horizontal to a vertical orientation. The X-Y table is composed of two connected stages with two degrees of freedom. The X stage can move along the X-axis. The Y stage is affixed to the X stage and can move along the Y-axis. The first mirror is fixed in an orientation with respect to the coaxial laser direction but not in its distance from the laser source, in other words the X Stage. The second laser mirror has a fixed orientation with respect to the first mirror and serves to redirect the laser beam to a direction antiparallel with the generated beam. This mirror is free to move in a direction

perpendicular to the coaxial as it is mounted on the Y-stage. The third mirror has a fixed orientation and distance from the second mirror and serves to direct the beam downward at a 90° angle. The focusing lens is directly below the last mirror at a distance that is variable in the vertical direction. The second and third mirrors as well as the focusing lens are mounted on the Y table, which is, in turn mounted on the X table.

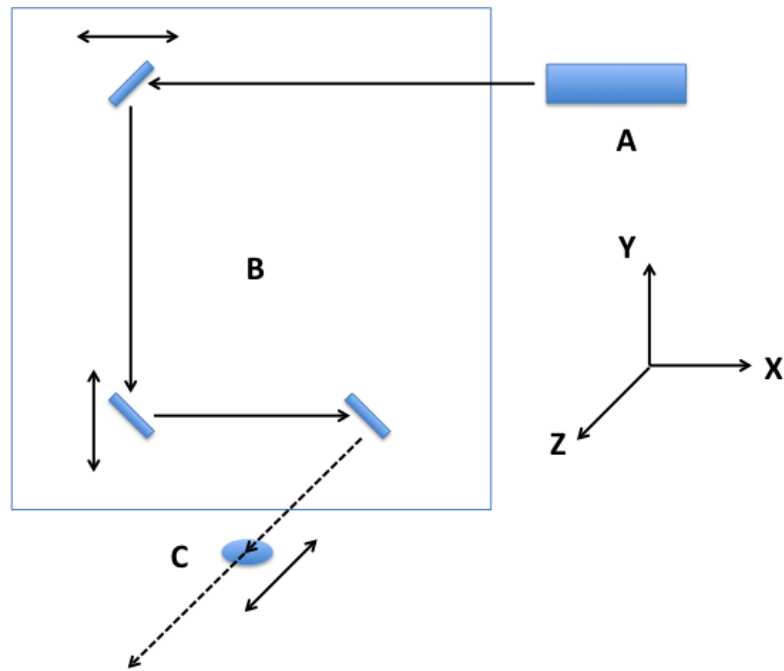


Figure: 6

Plan view of laser path. Dashed Z is downward, into the page. A is the collimated laser beam exiting the laser. B is the X-Y stage supporting the optical train and focusing lens C.

The X-Y Positioning stage is used to position the laser spot in any exact position on the substrate. The position of the laser spot is limited by, the envelope of the X-Y stage, and further limited by the size of the laser entrance window or viewport. Control of the X-Y stage is accomplished by computer control of two servomotors. The servomotor for each axis drives a lead screw, which converts the rotational motion into linear displacement. The pitches of the lead screw are extremely fine and can be used for micron scale

resolution of the stage positioning. A servomotor drives each screw and each servomotor has an encoder affixed. The encoders used are optical type, four channel, encoders that give a resolution of 8000 counts per revolution. 15.6 counts of the lead screw encoder will move the axis 1 micron. With an error of approximately 8 counts, the X-Y stage can be positioned to within 0.5 microns of the desired location. DC Servo motors were chosen for motion control due to their high degree of position control. Stepper motors were considered but stepper motors are limited by their step size. Encoded servomotors, while also limited to the encoder step size, can be controlled with a PID control loop.

A preexisting deposition system was designed for SALDVI specific experiments of silicon carbide. In order to get a large volume of gas, the reaction chamber was 300 liters in volume. The configuration of the chamber allowed for the manipulation of powder to create freeform deposition shapes. The excessive volume of the chamber was difficult to work with and the deposition system was not configured for ceramic joining. A system redesign incorporated several features. The potential for the addition of multiple liquid precursors as well as gaseous precursors was designed for. Some potential precursors with low room temperature vapor pressures would not be useable in the system without system heating. The large reaction chamber could not be readily heated without extensive modifications. A new chamber was designed and built, with a smaller volume of reaction gasses. This chamber could be heated with the addition of variac controlled heating tape. In order to have enough gas for productive decomposition reactions, an expansion tank was designed. A liquid precursor could be heated to an elevated temperature in a heated water bath. The vapor phase precursor would be stored in an

expansion tank that is heated. Pressure monitoring of the reaction chamber and the expansion chamber was done through the use of dual electronic pressure gauges. The first iteration of the system is shown schematically below.

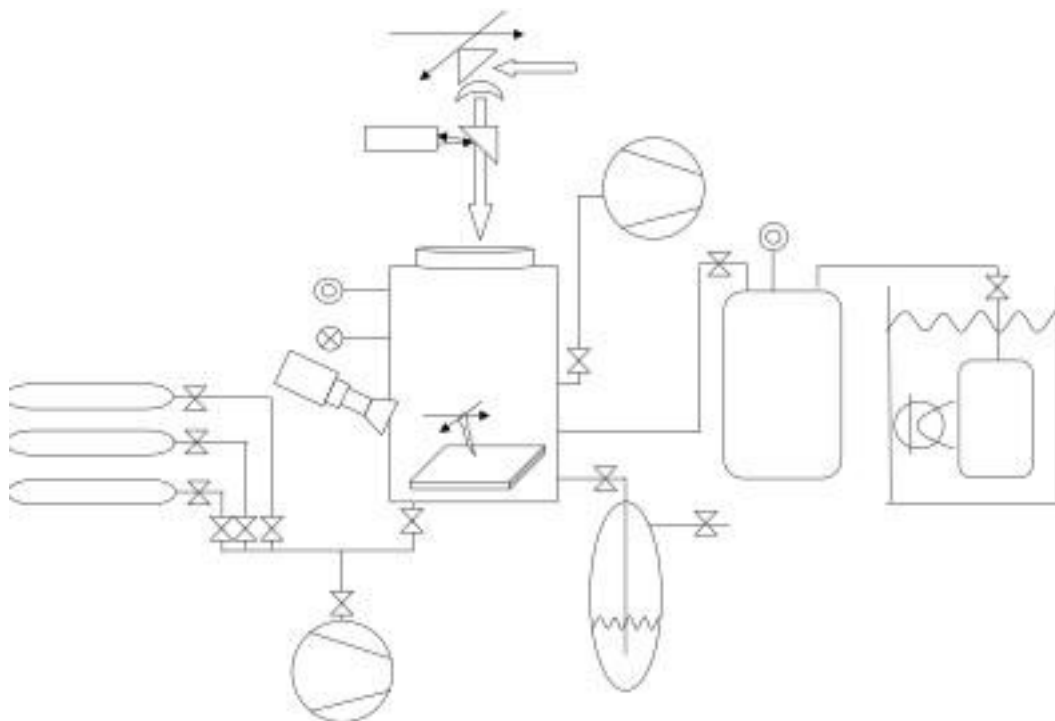


Figure: 7

Schematic representation of a heated reaction chamber is shown. This is the original design, which has been modified in several iterations. A small volume was chosen for ease of heating though the gas handling proved difficult to heat uniformly.

The difficulty of uniform heating of the reaction chamber peripherals as well as a need for a greater volume of reaction gas influenced the next design iteration. A simpler chamber with larger cross section was designed and constructed. A volume of 10 liters

was chosen for the reaction chamber allowing depositions with a volume of several cubic mm, depending on the precursors used. To heat the chamber for deposition experiments and bake-outs a smooth cylindrical main chamber was chosen so that a series of two part ring heaters could be attached. A dedicated temperature control unit with 7 channels and PID type temperature feedback controlled ring heaters.

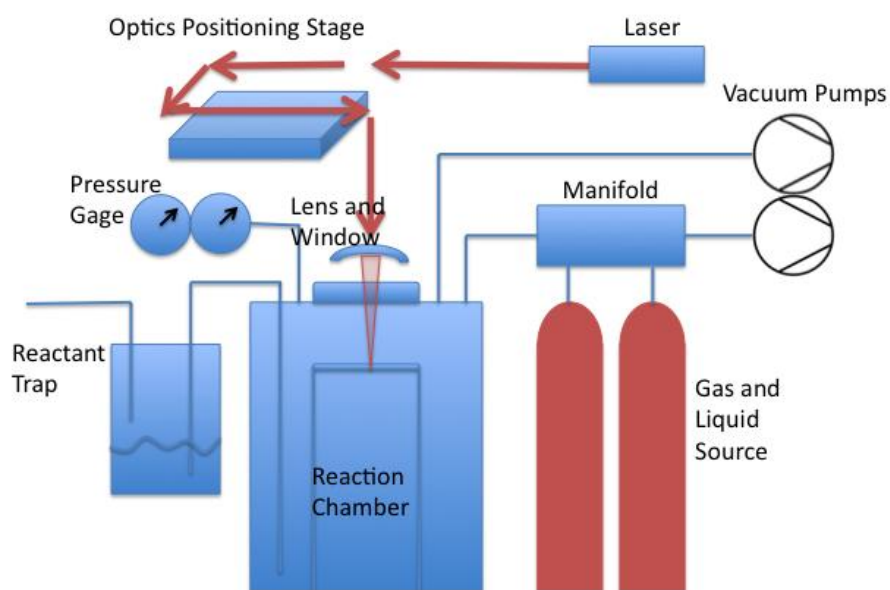


Figure: 8

Schematic of 10-liter reaction chamber and peripherals is shown above.

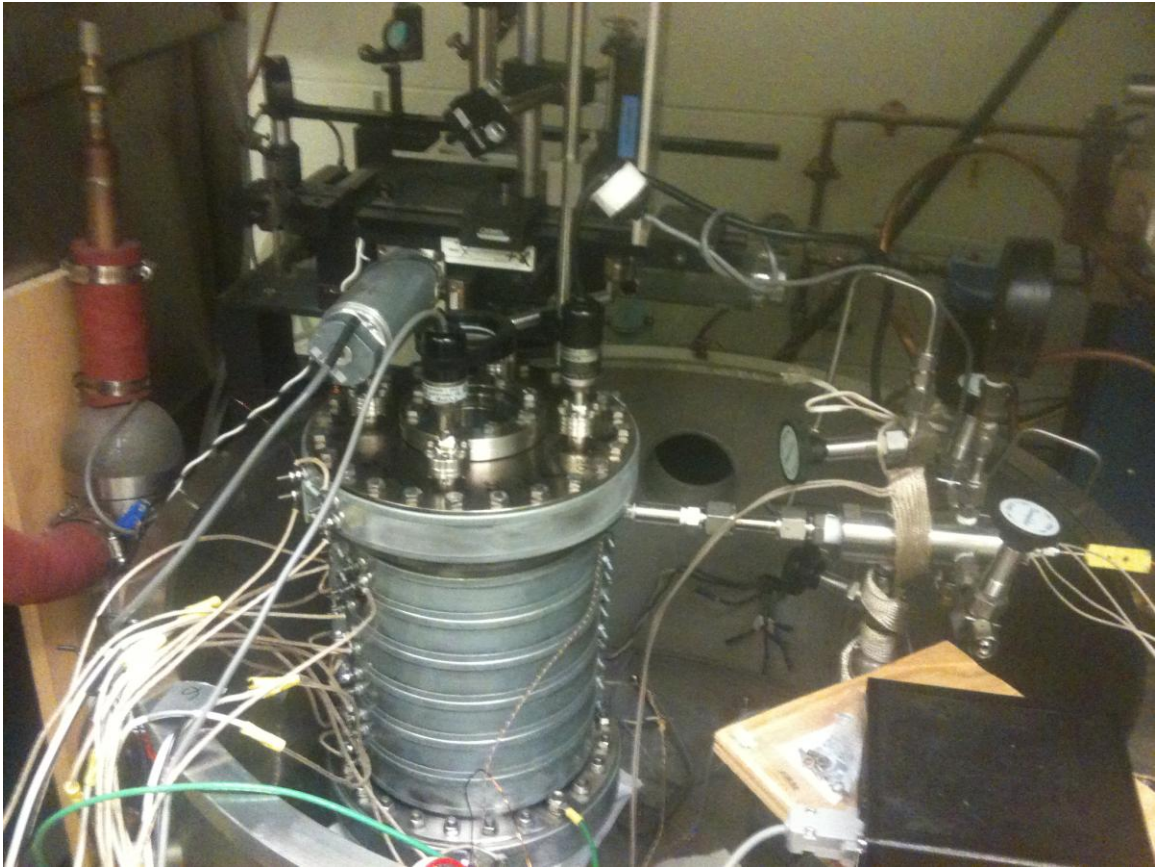


Figure: 9

The most modern deposition system is shown. A indicates the X-Y optics positioning stage. B is the reaction chamber with band heaters. The laser viewport, pressure sensors and focusing lens is indicated by C. D is the gas manifold for inputting process gasses.



Figure: 10

The gas manifold is shown. Process gasses lead to the manifold from external gas tanks. This manifold is capable of having two liquid precursor containers. A residual gas analysis and leak detection port is available. A chamber vacuum valve is also present. Cartridge heaters can heat the whole manifold and a thermocouple reads the temperature inside the manifold. The manifold leads to the reaction chamber and to a secondary manifold for gas mixing.

Process monitoring is an important component of the deposition process. Pressure monitoring of the system is necessary throughout the SALD process. When evacuating and flushing the chamber before deposition it is important to be able to observe the lowest pressure achieved in the chamber. The evacuation process must reduce the presence of unwanted gasses. For the low range of the pressure monitoring a thermocouple gage is used. This type of gage uses a thermocouple junction in contact with a resistance-heated filament. As the system pressure decreases fewer gas molecules are available to remove heat from the filament. The pressure gauge gives a temperature reading of the filament, which in turn relates to the system total pressure. The function of thermocouple vacuum gages makes them insufficient for total system pressure monitoring. [27] These gages are considerably more accurate at the low end of the pressure range, below 2 torr. They are calibrated for use with nitrogen and are not accurate for other gasses. In order to more completely monitor the process gasses a diaphragm vacuum gage is used. The diaphragm gage is insensitive to the process gas used as the pressure is indirectly measured. A Stainless steel diaphragm moves in proportion to the chamber pressure and resistance of a strain gage varies on the outside of the vacuum area.

When heating the chamber, it was necessary to measure the chamber temperature. K type thermocouples were used in each heating zone of the metal reaction apparatus. In conjunction with band heaters and a PID temperature controller the thermocouples were used to keep a constant temperature or a steady ramp rate. Heating the chamber is necessary for certain deposition conditions as well as chamber bake out.

Laser monitoring is accomplished with an inline laser power meter. In order to control the deposition, desired laser power is evaluated against actual laser power. Early iterations of the deposition system used an optical pyrometer to evaluate laser spot temperature. The system was designed to use a PID feedback loop to control the laser power. A periodic sampling of spot temperature was taken and laser power was modulated to keep laser spot temperature consistent. [21] When the system was modified to use a highly focused YAG laser, the pyrometer pressure monitoring became unreliable, as the sampling area was too large. The laser power of the YAG laser has far fewer fluctuations than the CO₂ laser making power modifications less necessary to achieve uniform deposits.

An essential component of the SALD system is the computer control. In order to create arbitrary deposition shapes it is necessary to simultaneously control two actions, laser power modulation and X-Y positioning of the laser spot. Besides the servomotors and encoders other motion control hardware is necessary. The control computer uses a motion control card to send control signals to a series of amplifiers, one for each axis of motion. The control voltage is amplified to a drive voltage that is used to power the motor. Servomotors are controlled by the application of DC current. Voltage increase or decrease translates into motor speed and polarity translates into forward or reverse drive. Each motor must be treated as a spring with programmable spring constants. Each move of the motor must be controlled so as to minimize overshoot. In order for a motor to stop at a specific point, as indicated by the encoders, the polarity must be reversed in a

controlled manner. The reversal of polarity results in reverse motion. A series of oscillations can result that approximates a damped spring. In order for the system to make controlled moves at a controlled speed the servomotors are assigned constants that represent, stiffness, damping and feedback gain. [38] Once programmed, PID motion control uses encoder feedback to modulate the motor and achieve controlled stage positioning.

PID motion settings were programmed using the Labview Motion suite. This program interfaced directly with the motion controller card, National Instruments PCI-7344 4 axis servo and stepper controller, as well as acting as an intermediary between the Labview control code designed for the SALD system. The Motion code was used for motor and encoder configuration and for basic two-dimensional positioning moves. The Motion code was also used for secondary monitoring of the primary Labview code.

The control program for the SALD deposition program was designed and modified to achieve the optimal performance. Labview 8.2 is the programming environment used. This program uses visual programming commands to manipulate the programming environment. Labview was chosen as the controlling program because of its data acquisition and analysis capabilities. Programming modules exist that allow for integration with motion control hardware and data acquisition devices.

The Labview code has to control laser power and motion control. The two programs were written separately and combined into one program. Designed to operate

concurrently. The laser has several safety interlocks, physical and digital. The first interlock disables the laser if the laser safety curtain is opened. Programmatically it is necessary to send a modulation signal to the laser. 10 volts allows the laser to be on continuously. A waveform sent through the modulation channel will cycle the lasers power on and off. The modulation is still a form of CW lasing; pulse generation would require a peak power while the modulation is a square or sine wave energy profile. The laser must be initialized by a digital on switch and will not run unless the previous run cycle record is cleared from the system. The laser has several stop sequences. A laser stop button and a program termination code both shut off the laser. When the deposition program completes, the laser modulation is set to zero and the lasing is stopped. The laser operation has several control variables; modulation, duty cycle and laser power can be set. The possible laser power of the 100 Watt IPG laser is 10-100 W and can be any intermediate power between these values if a proportional voltage is sent. The control voltage for the laser power is from 1 to ten volts. The laser control portion of the Labview code converts the user inputs to voltages, which are read by the motion control card. The motion control card in this configuration acts as an input/output device. The motion card is connected to a break out box that interfaces with the laser terminal inputs, both command terminals and interlock terminals. The laser can be controlled externally, either through the command program written in Labview or through an RS232 interface. Once the laser is set to external control it can only be controlled by the Labview code.

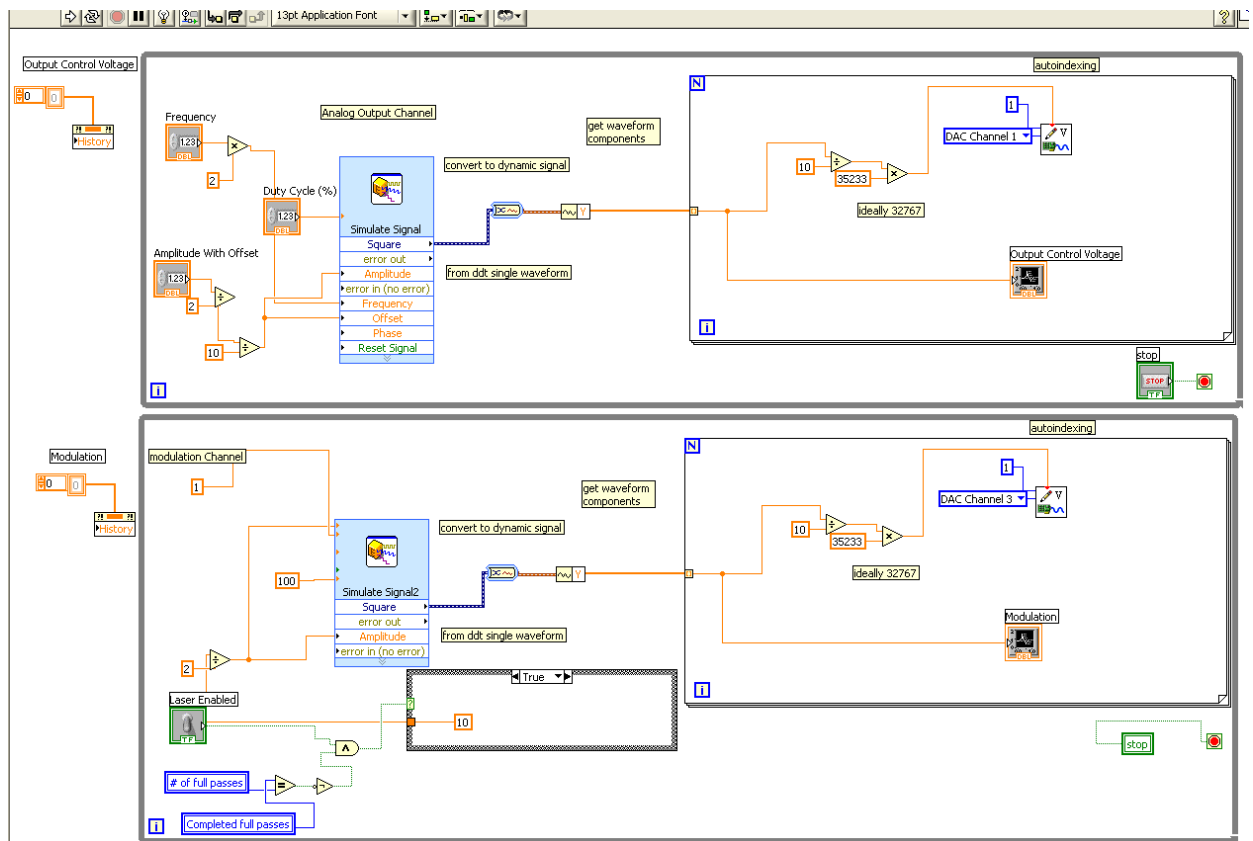


Figure: 11

Figure shows the Labview code written to control the laser power. The laser power, frequency, and duty cycle are controlled in this loop and signals indicating the laser status are processed. Two control loops are shown, with one block of code controlling the laser output control voltage and the other controlling the modulation and safety interlock channel.

System motion is controlled by a different section of Labview code. In order to relate motion commands to the servomotors, all moves must be described in a virtual vector space. The lines and arcs that comprise the complex motions of the deposition process

are represented as position and velocity information. Motion specific subroutines are used to program the behavior of the servos. Axes and vector space are defined and moves are blended from one vector to the next. To fully describe the motion, accelerations and velocities for each move are inputted.

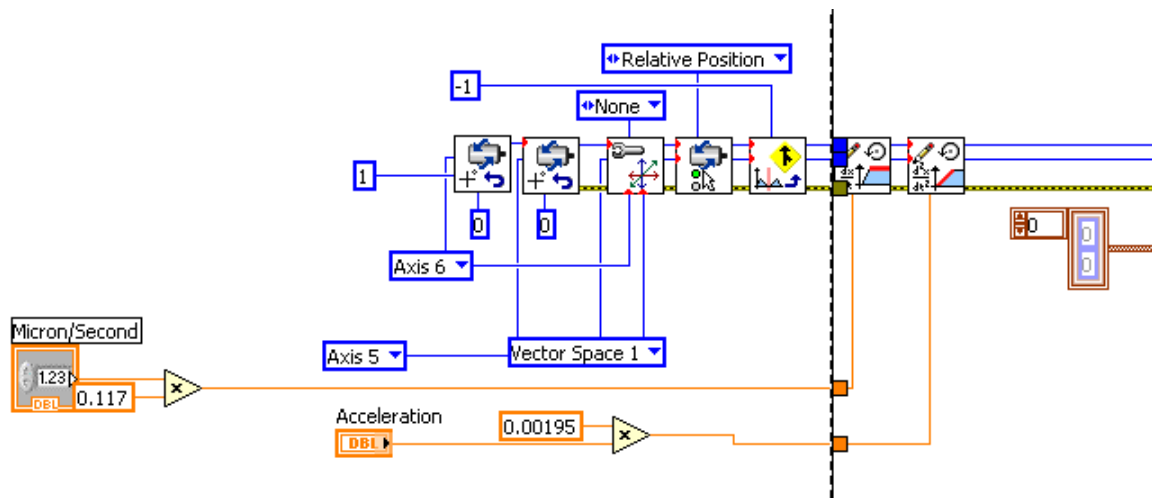


Figure: 12

Motor and vector space initialization sequence is shown. Axes are selected and the vector space they operate in is indicated. All defined moves are relative to the last completed move as apposed to true origin. Each vector is blended with the move before to create a smooth pattern. Acceleration and velocity are chosen.

The motion control portion of the Labview code executes a series of lines and arcs that together form the desired deposition pattern. The system is set up to perform joining type depositions that consist of various raster sections of different orientation and overlap. A predetermined pattern is entered as a series of discreet motions. The program treats line motion and arc motion differently, so the type of move is indicated. The code concurrently sends signals to the motion control board and to a position plotter so that moves of the servos are mirrored on the computer screen. Each deposition layer is

represented, in the control program, by a unique block of code. The raster pattern defined, can be repeated as many times as is necessary, to fill the desired deposition area. If more complicated deposition patterns are needed, the control program can be modified to accept a series of coordinates corresponding to an AutoCAD or similar input file. If a complex freeform shape is to be created, the line and arc section is replaced with an array of points and vectors defining the path from point to point. The deposition program plots the intended deposition pattern while the Measurement and Automation Explorer, MAX processes the real-time position of the X-Y stage.

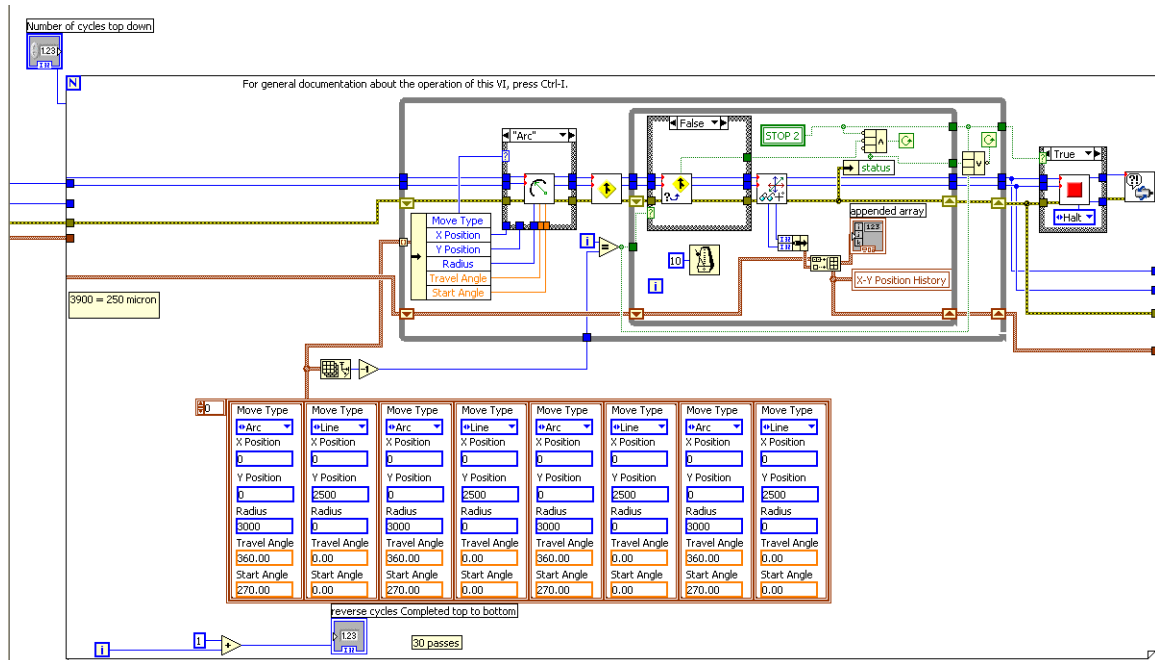


Figure: 13

The motion control portion of the code is shown. This code represents one in a series of repeatable deposition patterns. An Array of linear and curvilinear moves are inputted into a code that executes these moves by selecting linear or arc motion. Each vector is blended into the next to smooth the pattern. The move signal is transmitted to the motion card and then to the servomotor. The motion card processes encoder signals and a return signal is sent to the motion code where the completion of the move is confirmed. The next move will initiate after this confirmation. The code also concurrently plots the intended motion.

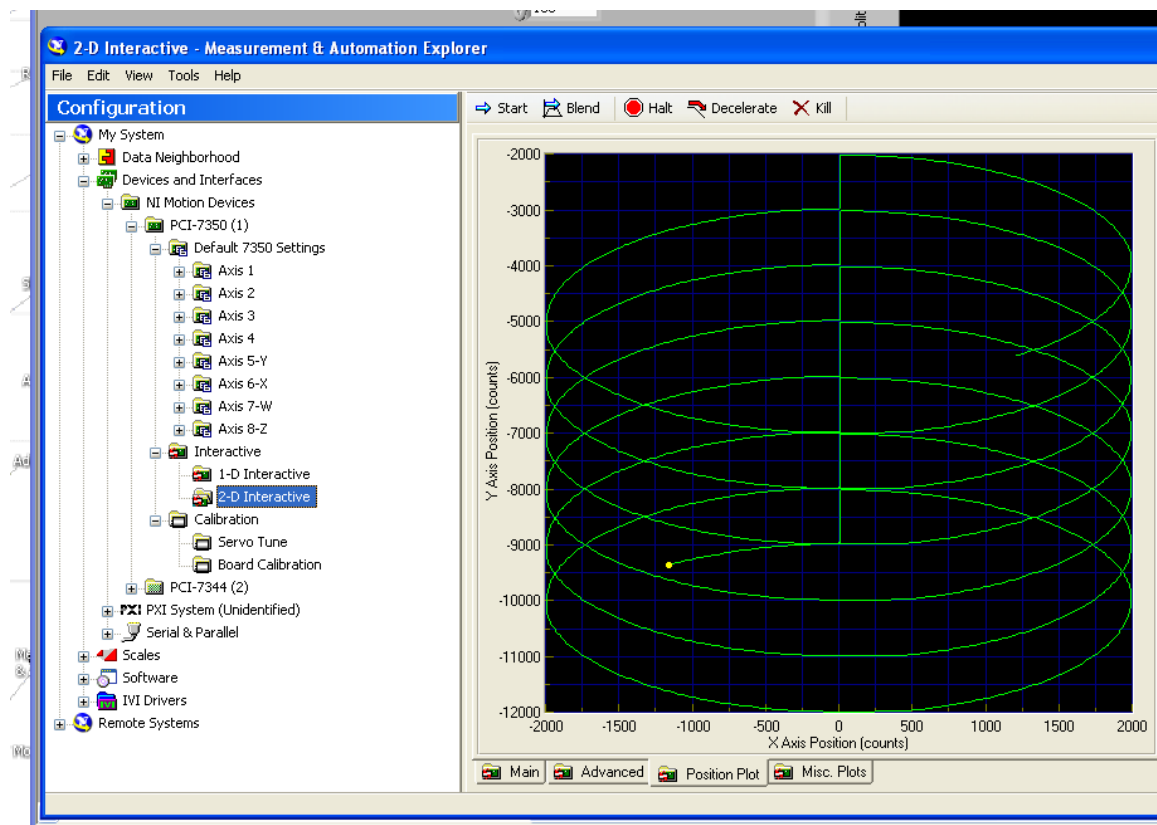


Figure: 14

Real time process monitoring of the encoder feedback. The true position of the X-Y stage is shown. The MAX program is used to manually control the system axes and position the laser before the automated program is initialized.

System evaluation and silicon carbide test deposits

Silicon carbide has been well studied as a SALD and SALDVI material. Experiments with the silicon carbide were performed with several objectives. SiC is a proven material

and the use of tetramethylsilane as a precursor is well documented. Experiments were done to reproduce some of the previous research, as a test of the capabilities of the deposition apparatus, and to demonstrate the ability to join planar silicon carbide specimens.

There are several parameters that can be varied during the deposition runs. These parameters include: gas composition and mixture ratios, laser power, focus and modulation, number of passes per layer of SFF structure, temperature of the chamber, and laser scan speed. The test of the system was performed with the following parameters held constant: laser power, modulation (duty cycle), and gas concentration. The aim of the experiments was to vary several parameters and then to repeat the experiments at a series of elevated temperatures.

A laser power of 3.5 watts, CW, generated from a 1070 nm fiber laser, was used with a focused spot of 90 micron. The substrate was 3mm thick sandblasted Titanium.

Reaction Gasses used were, 50 torr TMS, 300 torr Helium, and 50 torr Hydrogen. Scan Speeds of 10, 50, 250, and 1250 microns per second were used in combination with 1, 5, and 10 superimposed scans per line. The objective of the tests was to vary scan speed and number of passes over the same spot, in order to understand the deposition characteristics on this substrate. This information would then be used for the construction of multiple layered arbitrary shapes of Silicon Carbide. Deposition results are summarized below.

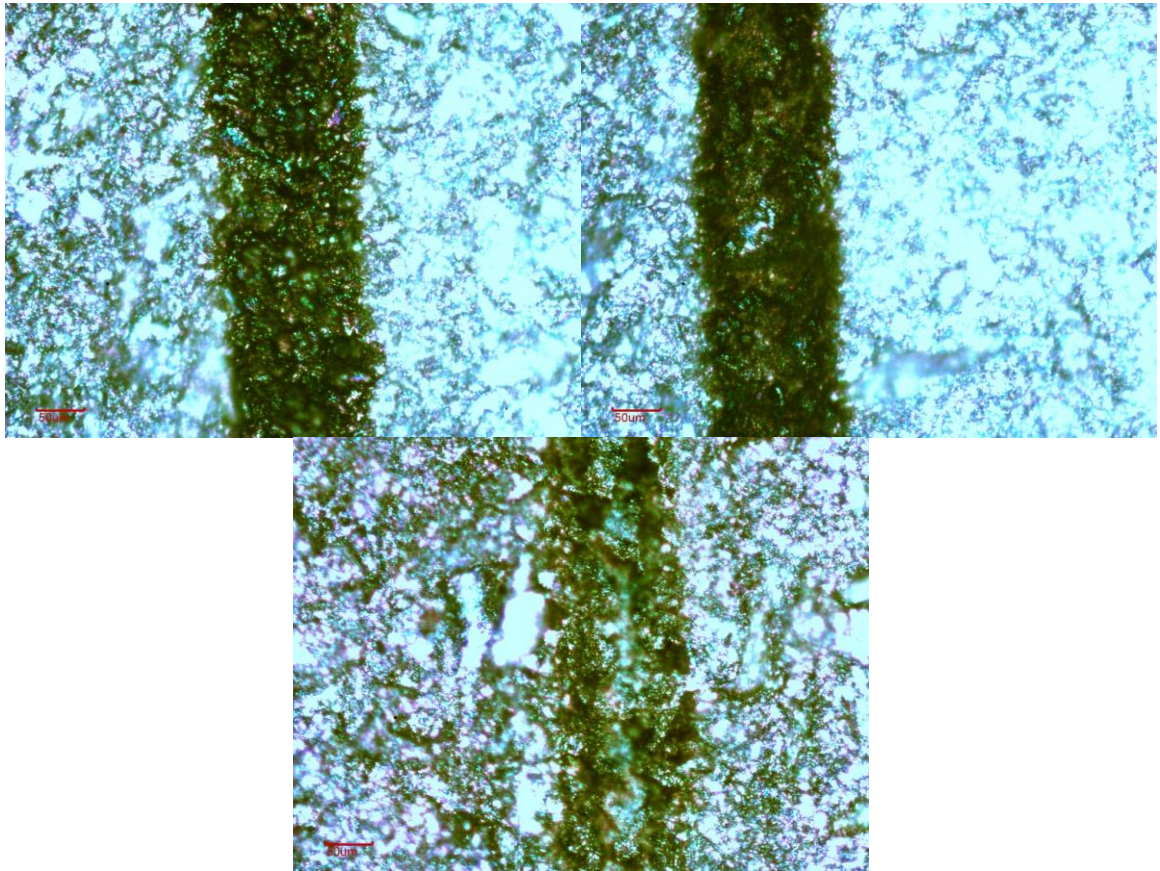


Figure: 15

Single layer deposition runs of SiC on Titanium with scan speed varying from left to right, 10, 50 and 250 microns/ second. Visible light microscopy was used with a 20X objective.

The scan speeds above resulted in very fine deposits, well bonded to the titanium substrate. The scan speed of 50 microns per second resulted in the most even deposition

across the beam profile. The scan speed of 250 microns per second resulted in the thinnest deposition layer above although a speed of 1250 microns per second was also tested and resulted in an uneven and very light deposition not easily imaged by optical microscopy.

250 microns per second was chosen as the scan speed to test multiple co-spatial passes of 5 and 10 passes per line. In this case the positioning capabilities were also tested. The images below are segments of 2 mm radius circles of SiC deposited onto Titanium substrates.

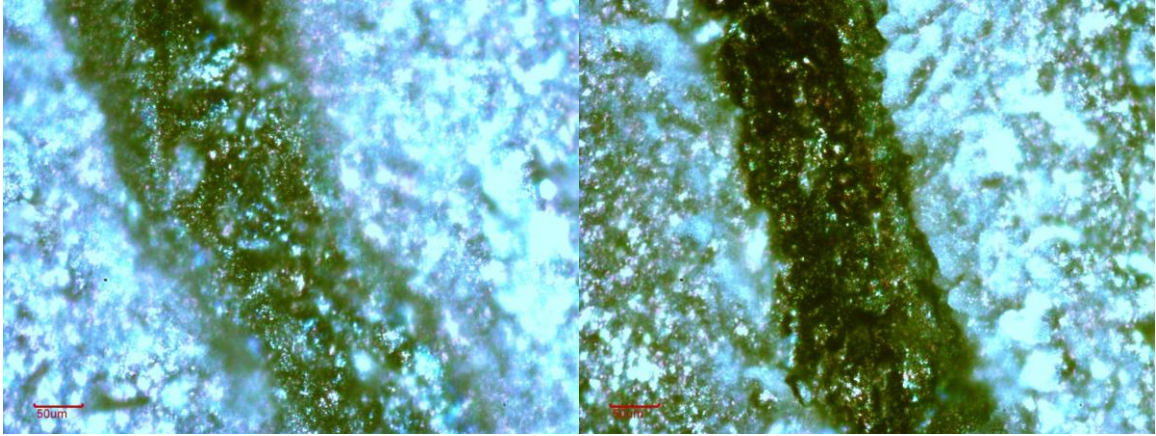


Figure: 16

Both depositions above were made with a scan speed of 250 microns per second.

The left deposition was made with five consecutive passes of the laser and the right deposition was made with 10 consecutive passes.

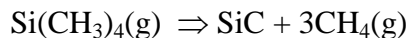
The highest scan speed, of the three viable scan speeds, was chosen because multiple passes at the lowest scan speed resulted in runaway growth. This runaway growth resulted from excessive heating of a small protrusion, which then grew upward and away from the surface.

The test of the heated chamber showed that the chamber could be maintained at a temperature of 50 C with a variation of ± 5 degrees over the different temperature zones.

Ceramic Joining of Silicon Carbide

Introduction

Ceramic joining of components can be done by several methods. Green pieces can be joined ultrasonically before firing, frictional joining or the use of brazing materials can be used if the components are already fabricated. These methods involve special conditions that must be considered before component design. Another method that has been studied is the use of a focused laser in a reactive gas environment to selectively heat a substrate and decompose the ceramic precursor and form a joint. [1][2][7][12] This process, known as selective area laser deposition (SALD), can be performed without bulk heating of the components and without the use of materials that will be ineffective at higher temperatures. The SALD has been used with some success to join components with a rotational symmetry. [10] A variant of the SALD process that involves the infiltration of a substrate powder with precursor gas during decomposition is known as the SALDVI process where the VI indicates vapor infiltration. This technique has been used for free form fabrication of arbitrarily shaped components. The powder that is to be infiltrated can be the same material as the decomposed species or a different material making a composite. Several types of ceramics have been fabricated with the SALD and SALDVI process including Si_3N_4 , graphite and composite materials utilizing different metallic and ceramic powder reinforcements. This study utilizes Tetramethylsilane ($\text{Si}(\text{CH}_3)_4$) pyrolytic decomposition in the presence of hydrogen in the overall process reaction:



Alternative precursors to form SiC include methyltrichlorosilane (MTS , SiCH_3Cl_3), and combination of silane (SiH_4) and methane (CH_4). [3][8][15][24]

Experimental Procedure

Previous joining work has concentrated on the use of deposition without the use of a powder to infiltrate. This study combines the use of SALDVI with the previously established joining techniques. A 40-watt average power pulsed fiber laser with 1.5 mJ per pulse (SPI Lasers) was used for the studies. A single focusing lens was used with a focused spot of 50 microns. The beam was delivered off of a series of mirrors on an XY motion stage controlled by a Labview motion program and a National Instruments control card. The deposition chamber is a vacuum chamber flushed with argon and evacuated to 80 mtorr and then filled with desired gas proportions. The starting gas operating pressure for all experiments was 50 torr TMS and 50 torr H_2 , below the vapor pressure of TMS, to prevent condensation within the chamber. Semi Infinite powder bed deposition was used to evaluate deposition conditions using a 7-micron average size SiC powder. Laser powers of 20 and 38 watts average were used with laser scan speeds of 100, 200, and 400 microns/s. The higher power at all speeds ejected considerable powder from the point of focus leaving trenches in the powder with deposits into the trench walls. With the lower power the most consistent deposit was produced at 100 micron/s. To determine the spacing to be used for the joint deposition raster pattern, powder bed deposits were made with decreasing line spacing from 1800 microns to 80 microns. A powder bed raster

deposit was made 1.5 mm wide with a scan line spacing of 85 microns and a total length of 6 mm and a scan speed of 100 micron/s at 20 watts average power.

Achieving the correct laser parameters for a successful deposition is an exercise in compromise. If the laser focus is too fine and the laser power is not greatly reduced there is the potential for substrate ablation. This ablation occurs when using a pulsed laser, but can be used to create mechanical keying between the substrate and the deposit. The ablation can then occur with the deposited material, which is counterproductive to the deposition process. Achieving the correct laser spot temperature for deposition results in an area, surrounding the laser spot, that is heated but not to the full decomposition temperature. Partial decomposition can result, leaving non-stoichiometric deposits that decrease the quality of the final deposit. Subsequent laser passes can greatly reduce this contamination. A laser raster pattern that passes over each spot multiple times decreases the effect of this contamination. Determining the correct laser spot overlap helps to create a deposit with increased density.

The joint configuration explored was an abutting of two beveled edges with a powder fill of 7-micron SiC powder, packed into the joint cavity by ultrasonic vibration. A joint component thickness was chosen so that the depth of penetration of the laser into a free powder bed was equivalent to the SiC plate. A parallel rectangular raster pattern was chosen with a line spacing of 130 microns in the travel direction. The deposited width of

the raster pattern was designed as 130% of the largest part of the joint gap. The sample geometry used in this study is indicated below, Figure 17.

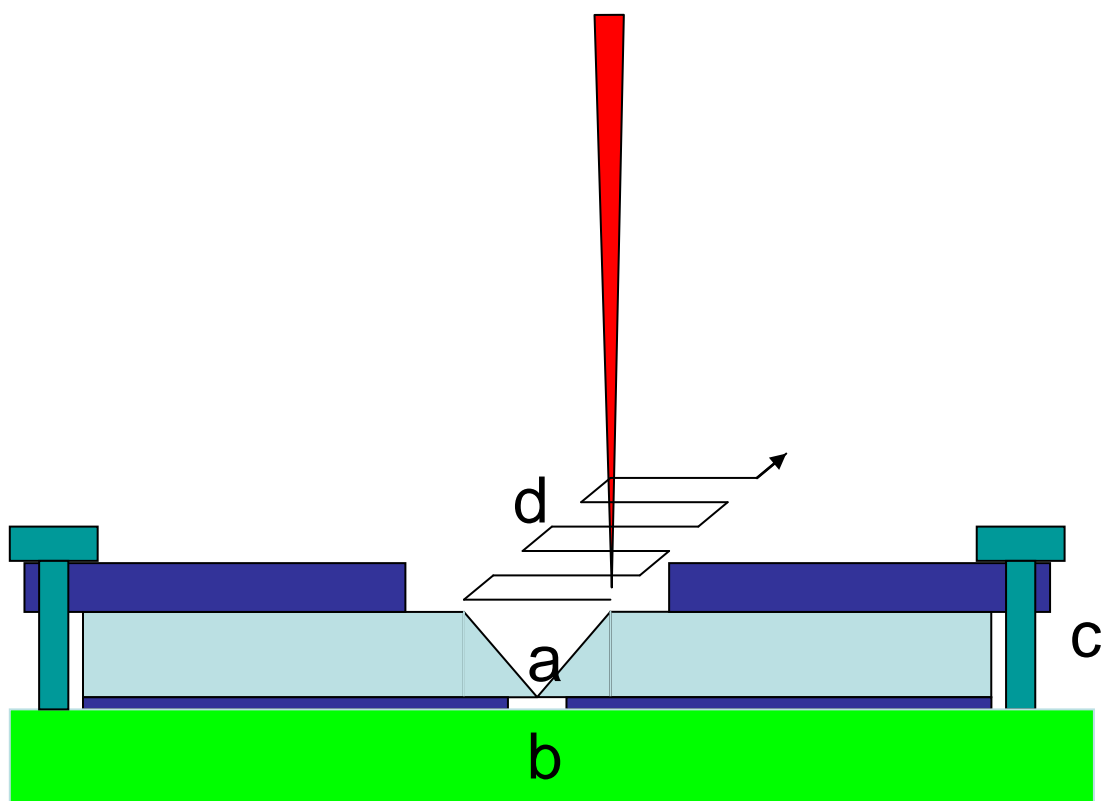


Figure: 17

Schematic of sample configuration: a. Beveled SiC plates 1270 micron thick with standardized 20° bevels. b. Diffusion gap created by spacers to allow diffusion of reactant as well as a measure so the joint would not adhere to the sample mount. c. Mounting clamp that secures each beveled section. d. Rectangular raster beam path.

The two beveled SiC plates were abutted and clamped onto a sample stage. The samples were separated from the sample stage by thin sheet steel spacers to prevent any adhesion to the stage and to allow for possible diffusion of the reactant species to the non-beveled

side of the joint. Two variations of the joint were evaluated, both were formed with a 50 micron spot size scanned raster with a 20 watt average power with a starting TMS pressure of 50 torr, H₂ pressure of 50 torr, and a scan speed of 100 micron/s. The first joint fabrication type was performed with no joint surface preparation. The second joint was formed by pre ablating the faces of the joint components without the presence of powder or reactive gas in order to produce a micro textured surface and then filling the joint cavity with powder and performing the SALDVI process as had been performed in the joint type 1. Analysis of the deposited material was performed with the use of visible light microscopy, environmental scanning electron microscopy as well as X-ray diffraction.

Results and Discussion

The decomposition of TMS in this study has two general microstructural types. The SiC formed by the infiltration of the powder and the SiC that has formed either by displacing powder or by decomposing on already infiltrated powder. The powder infiltration deposit type is seen below:

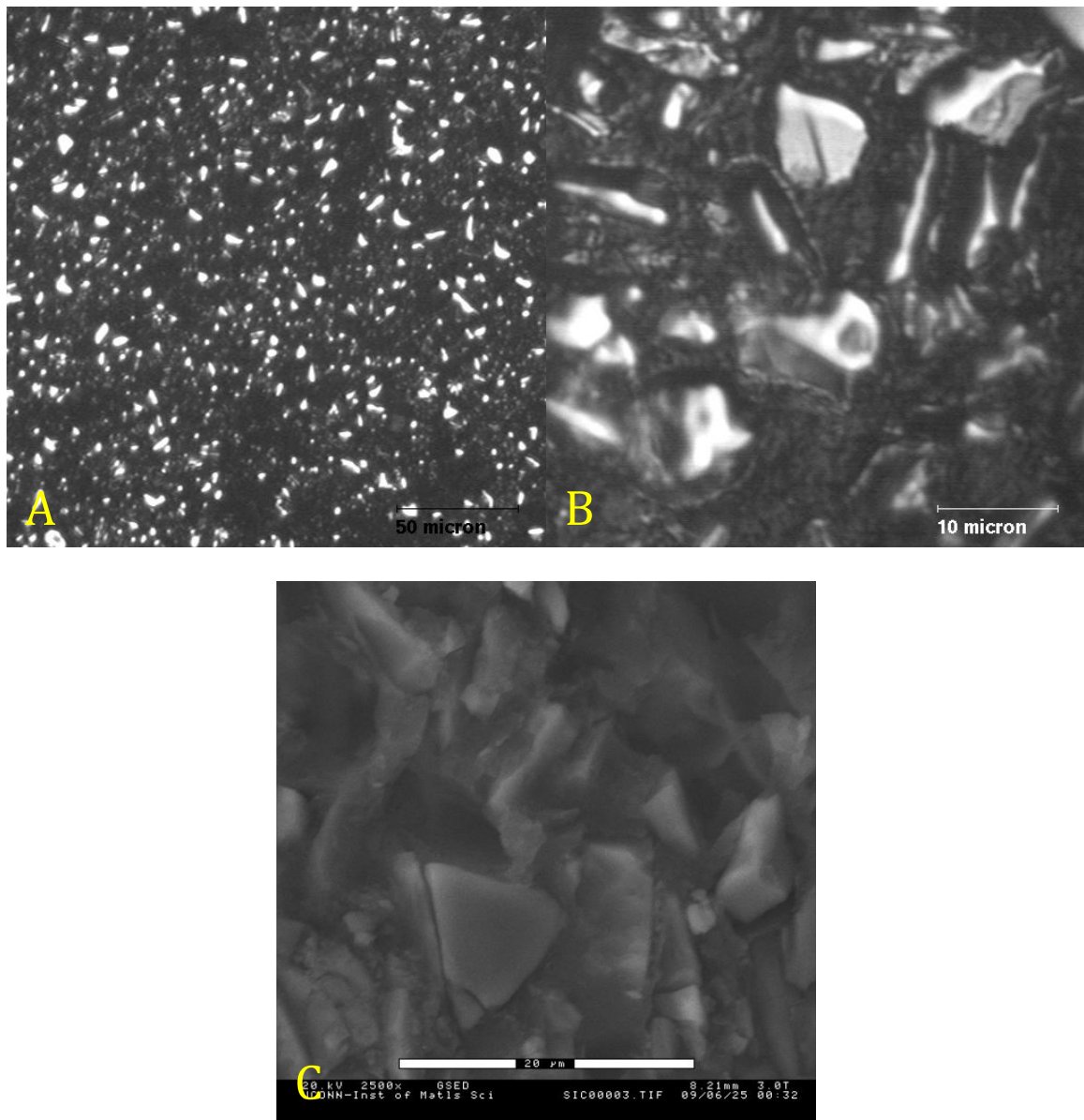


Figure: 18

The decomposition product has surrounded the SiC grains with a somewhat dense deposit. a. Infiltrated powder at 25X visible light magnification taken from a progressive line spacing scan in a region of uniform deposition. b. a 125X visible light image taken from an infiltrated region of a joint sample. c. an ESEM image of a powder bed scanned deposit at 2500X magnification

When infiltration paths into the powder bed are closed by the growth of the SiC deposit, a condition arises that allows SALD to occur, deposition without infiltration, Figure 19.

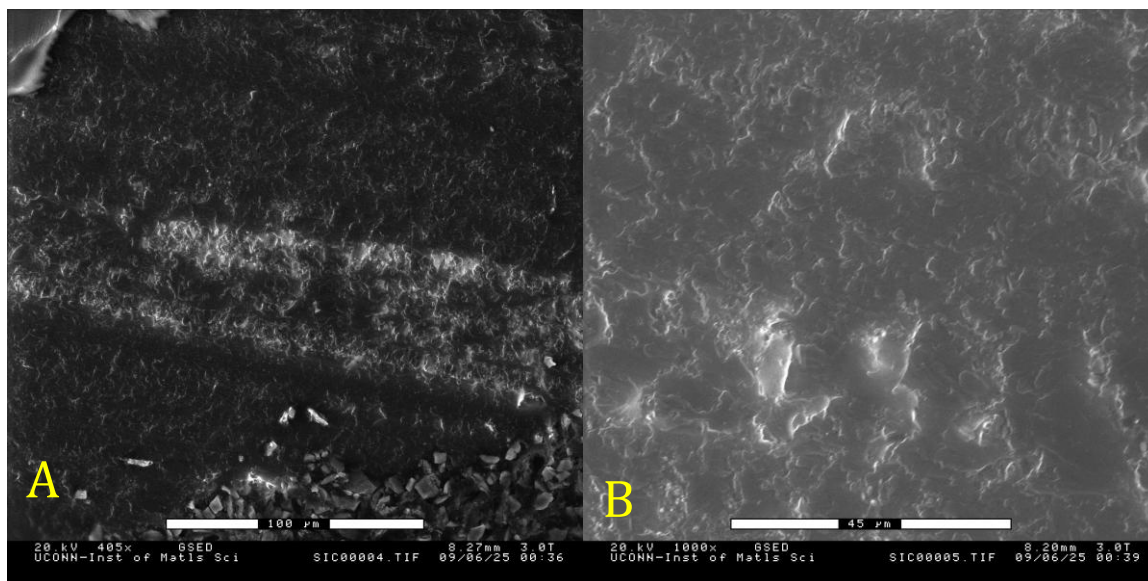


Figure: 19

These images are representative of the decompositions that occur without powder infiltration. a. an ESEM image at a magnification of 405X of the deposit above the powder bed. Image b is a higher magnification, 1000X, of the same region above the powder. Reasonable densities are observed.

To determine the optimal spacing for the parallel lines of the raster pattern a deposition was performed with variable line spacing. The factors considered for optimal spacing were: uniformity of the deposit in the vicinity of a scanned line, the extent to which an adjacent line was resolvable and the presence of beam damage. Light microscopy was used to evaluate the beam spacing, Figure 20.

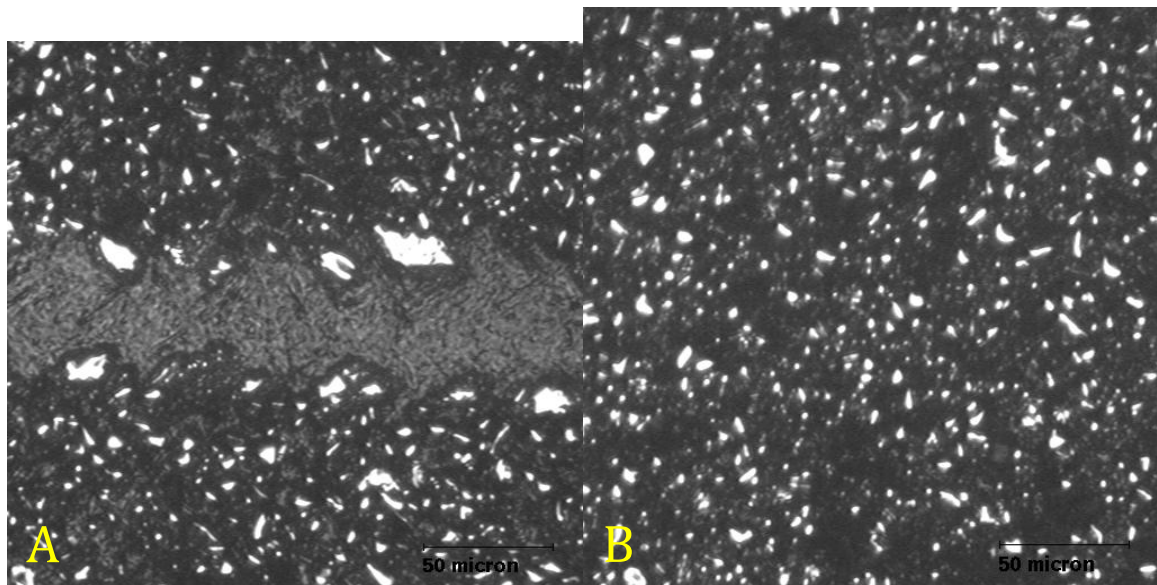


Figure: 20

The proximity of one line to the next in the powder bed deposition, affects the quality of the deposit. a. the central line is epoxy material which has filled the space left by the laser powder displacement and this micrograph represents the most widely spaced scan width (1.8mm). b. An intermediary scan spacing (300 microns).

The spacings of the raster lines that produced the most uniform deposits were found to be in the range of 300-80 micron. Deposition into a powder bed with a raster pattern with line spacing of 85 microns was performed on a semi-infinite powder bed. Resulting in a cohesive unit of good uniformity and reasonable density.

Deposition for the purpose of joint formation was performed. The goal of the joining studies is the formation of a strong and minimally porous joint with a full penetration to the base of the joint, with good cohesion to the joint wall. Two joining techniques were attempted. Joint type 1 is characterized by flat joint wall surface prepared by diamond grinding (to 220 grit). Joint type 2 was laser scribed by the fiber laser in order to provide a surface roughness. Previous joining attempts were met with greater success when the joining surfaces showed some porosity. [55]

The porosity of each joint was qualitatively evaluated by the ESEM. The initial particle size for the substrate powder is less than 7 microns. The structure of the deposition indicates the growth of SiC surrounding the particles, Figure 21.

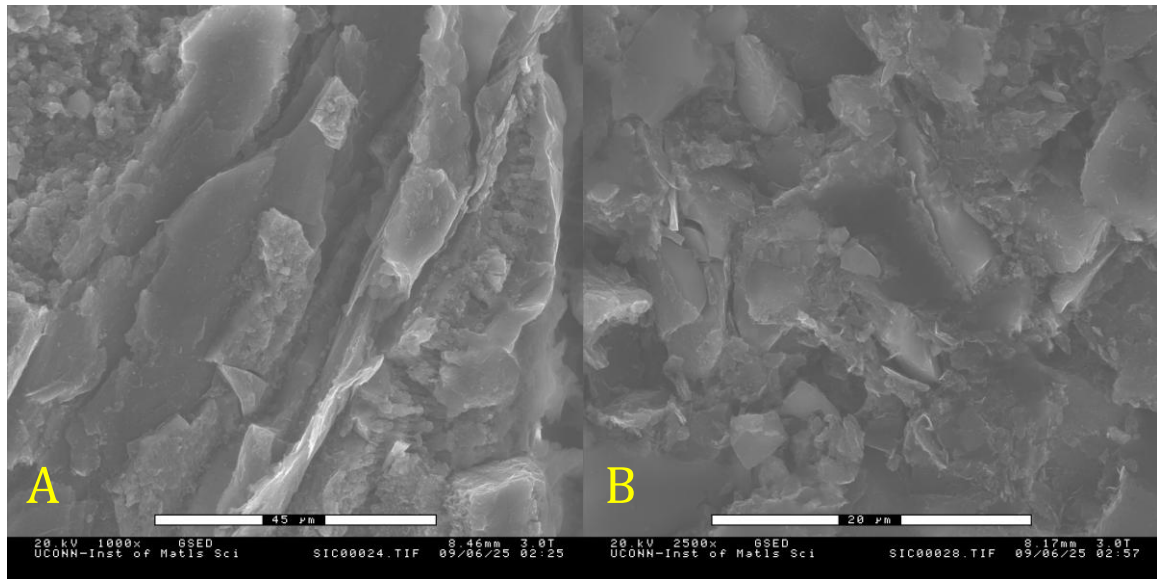


Figure: 21

a. Deposited joint material with a 1000 X magnification that displays a region of partially reacted powder in the upper left next to a larger region of deposited material. It can be seen that deposition was occurring with some irregularity in this sample, joint type 1. Image b taken from a sample of joint type 2 at a magnification of 2500 X displays a more uniform deposition with no regions of uncoated powder. Both images display reasonable density.

The use of a high quality beam source, in the form of a fiber laser, and a focusing optic with a 50-micron spot size, has allowed a deep penetration into the joint cavity.

Although both joints experienced a de-cohesion as a result of moments applied during the sample removal, the joint type 2 shows evidence of deep joint penetration. Although

fracture occurred along one deposition edge, the un-fractured edge shows little porosity at the boundary, Figure 22.

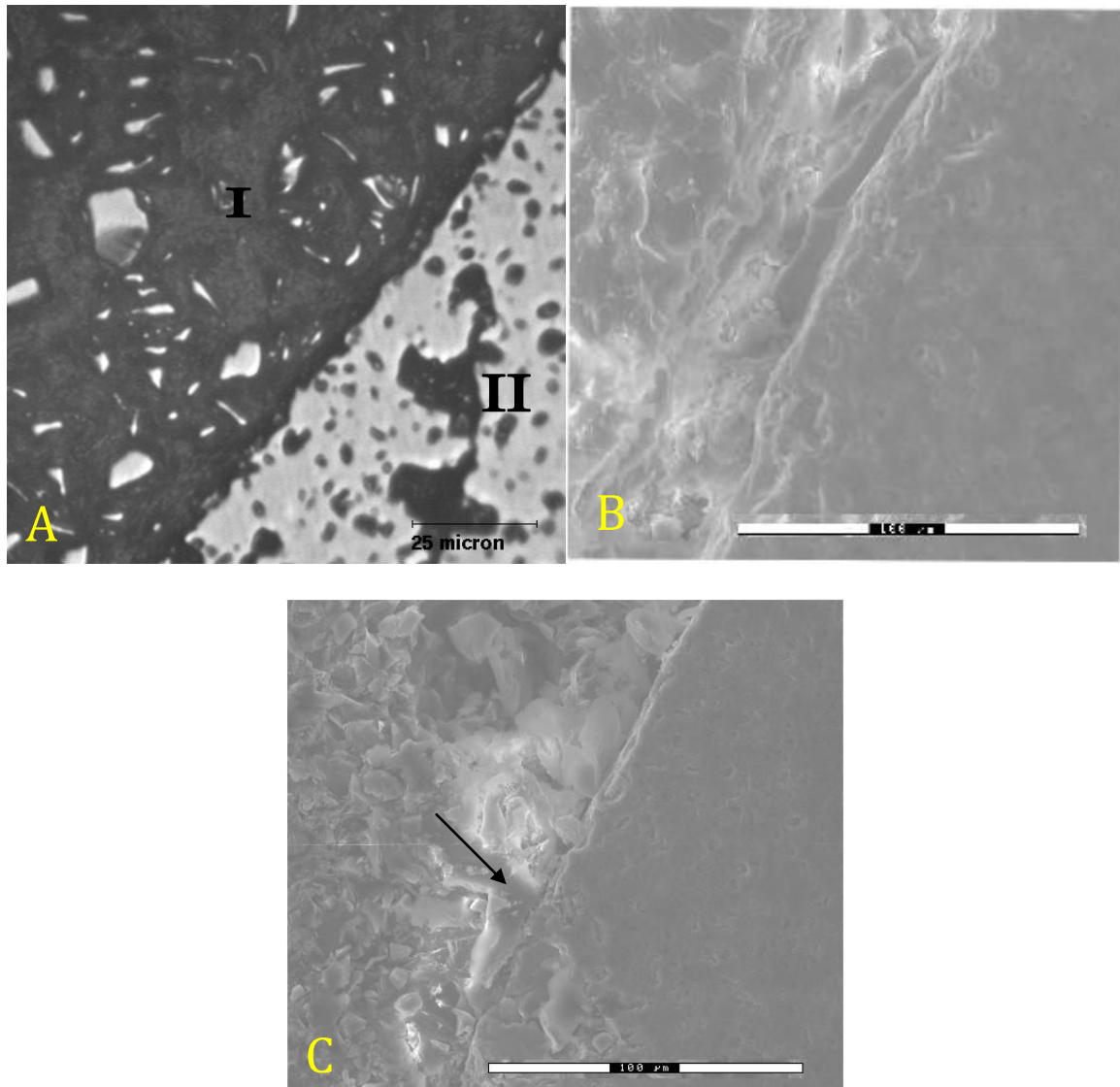


Figure: 22

a. A polished sample taken from a joint type 1 on an optical microscope with a magnification of 50X that shows a distinct and non-porous boundary between the deposit material, I, and the joint wall/substrate, II. ESEM images of Joints type 1 (b.), and Joint type 2 (c.) where both show the same type of adhesion at a magnification of 500X where the left side of each interface is the deposit. c.

shows a region, identified by an arrow, where the deposition material penetrated a micro ablation present from the laser pretreatment.

The beam penetration is evident from the deposited material in the presence of the crack tip. The joint type 1 joint did not have full penetration to the joint tip. There is evidence of deposited material at the tip of the second joint type, Figure 23.

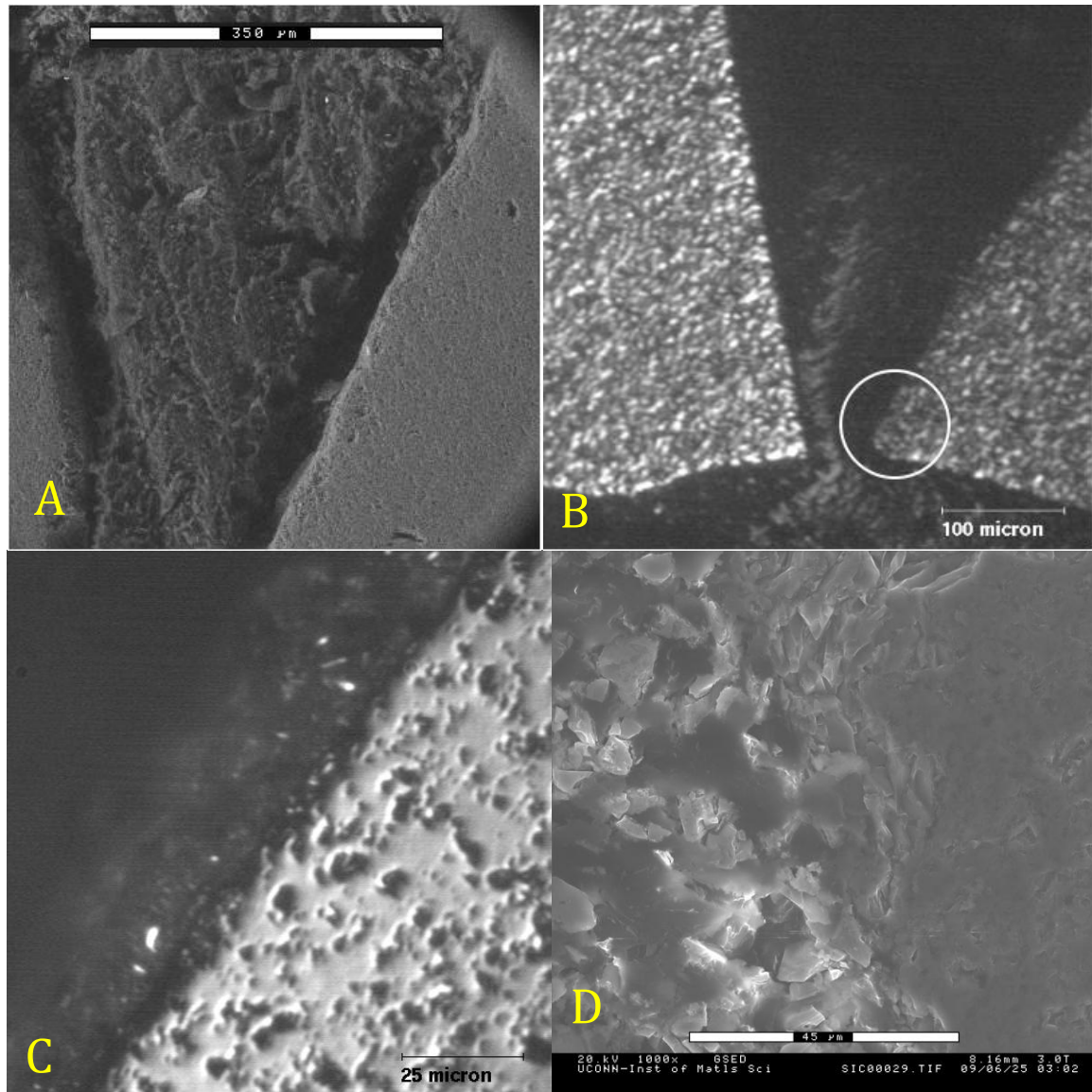


Figure: 23

a. Micrograph of the type 1 joint indicating partial penetration before joint fracture, image at a magnification of 125 X (backscattered ESEM). b. Optical micrograph (12.5 X magnification) of the type 2 joint penetration, the deposited material (black) is adhered to the joint tip. The grey material to the left of the circled region is infiltrated epoxy into the fracture zone. Image c is an optical

magnification of the same region at 50X magnification. Image d is an ESEM image with a magnification of 1000X. Image d also shows evidence of the laser pre ablation in the substrate tip, right.

Deposits were confirmed to be silicon carbide through the use of powder x-ray diffraction. The diffraction pattern standard for synthetic hexagonal silicon carbide corresponds closely to the experimental pattern as seen below, Figure 24.

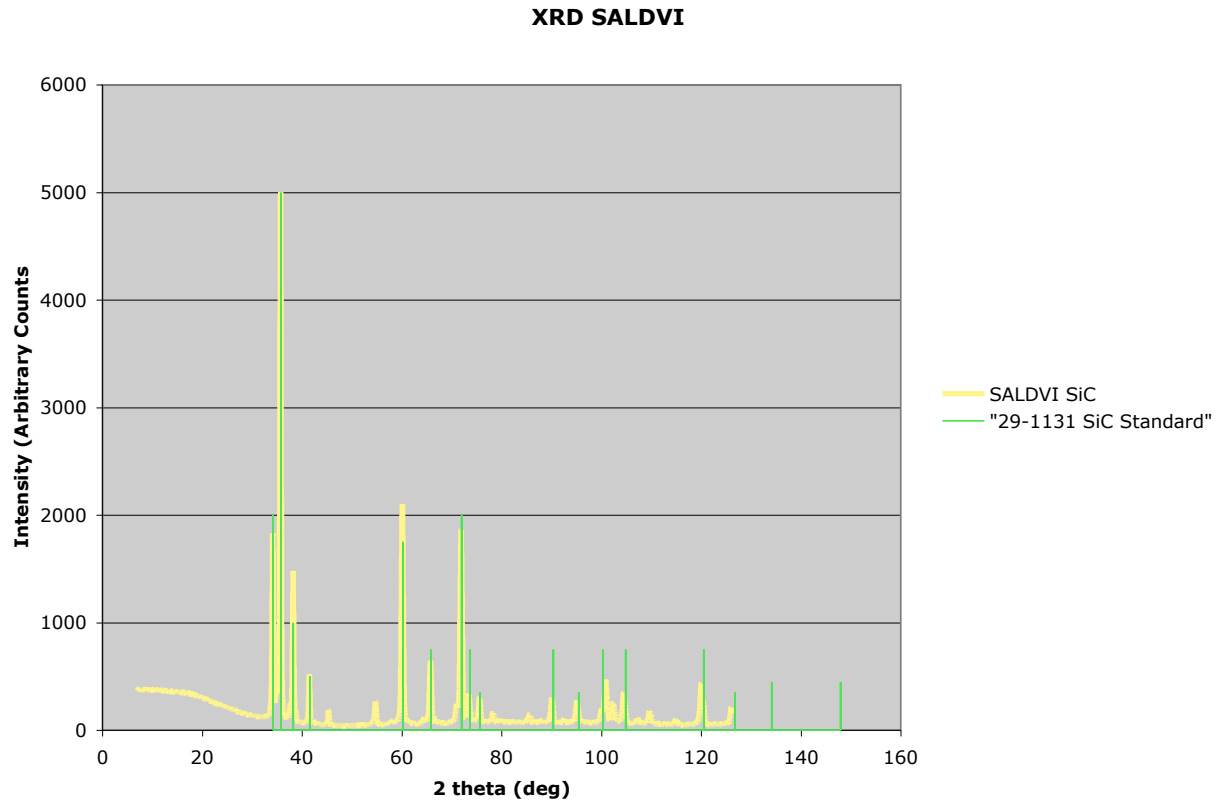


Figure: 24

X-Ray Diffraction pattern for the composite joint material compared with a standard for hexagonal SiC.

Conclusion

The novel technologies employed in this study include the use of a high quality fiber laser generated beam focused to 50 micron, the use of powder material filler phase within the joint, and the use of the laser as a means of ablating the surface of the joint before the infiltration process. The powder bed infiltration tests indicate that the beam is capable of penetrating the powder and decomposing the precursor to a uniform depth. If the sample

joint is kept to a thickness below that of the penetration depth a SALDVI type joint is possible. Thicker samples would necessitate a multi layer approach. The fiber beam shows promise for future joining studies but a balance must be reached between the desired penetration depth of the beam and the tendency for the beam to displace the powder from the hot zone. The surface pre ablation technique employed here was detectable under microscopic examination. There was deposited material within the ablation tracks. The ablation pattern was made under potentially oxidizing conditions, which could have been a factor in joint de-cohesion.

Selective Area Laser Deposition for Silicon Nitride Joining

Ceramic joining is a difficult step in ceramic manufacturing. Joining ceramics, in a chemically homogeneous way, can be performed through the repurposing of an additive manufacturing technique involving local deposition of ceramics from the gas phase.

Selective area laser deposition uses a gas phase precursor environment and a laser heat source to form ceramic deposits. These deposits can be positioned with great spatial resolution; as such, it is possible to form the joint with the ceramic material to create a monolithic structure. Silicon nitride is explored as a joining material for silicon nitride work pieces. The experimental conditions are described and the joint formation is characterized.

This study explores the process of utilizing SALD and SALDVI approaches to form silicon nitride joints of silicon nitride substrates. The experimental parameters that can

be manipulated, and the experimental setup used, are discussed. The resulting ceramic depositions and joints are characterized.

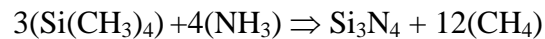
Chemistry Selection

The chemical composition of the deposited material is controlled by the chemistry of the precursor gasses. Some ceramic materials can be made through the pyrolytic decomposition of a single precursor while others require a more complex chemical reaction. Silicon carbide can be made through the decomposition of a single source, tetramethylsilane, TMS, $(\text{Si}(\text{CH}_3)_4)$, with the addition of hydrogen, to reduce carbon contamination and non reactive dilution gases. The reaction that defines the formation of silicon carbide is:



Hydrogen and helium are added in practice to minimize the formation of carbon. [56][14]

To form silicon nitride, Si_3N_4 , a combination of reactive gasses is required. The stoichiometric relationship for the formation of silicon nitride is as follows:



To promote the production of Si_3N_4 over SiC and SiCN an excess of ammonia is required. The relationship $f = \text{TMS}/(\text{TMS} + \text{NH}_3)$ can be used to indicate the relative

amounts of the reactants. The stoichiometric relationship yields an f of 0.43; however, it has been documented that for f less than 0.1 is required to drive the reaction to the production of relatively pure Si_3N_4 . Experiments were conducted using f values from 0.5 to 0.05 confirming the trend toward Si_3N_4 dominant composition. [16][17]

In practice the deposition of silicon nitride and other SALD deposits are best performed below atmospheric pressure in a partial vacuum. Besides the physical constraints of the system, the reaction chamber is designed for operation at below atmospheric pressure. It is necessary to keep the partial pressure of all reactants below their equilibrium partial pressure. If this is exceeded, reactant condensation will occur. In order to keep the correct concentration of ammonia and maintain the pressure below atmosphere it is necessary to keep the TMS at a lower partial pressure, which limits the available yield of Si_3N_4 . A balance must be maintained so that there is the greatest yield of the decomposition product while keeping the overall pressure below atmospheric pressure. The initial total pressure must be kept sufficiently low as the yield of product gasses is in excess of the initial gases by a ratio of 12:7. If the total pressure becomes high enough, of the order of atmospheric pressure, a contamination film tended to form on the chamber window interfering with the laser beam.

Experimental Set Up

The SALD/SALDVI deposition system is ~10 liter vacuum chamber with a centrally located laser window. A sample stage is located beneath the window with various

sample fixturing positions. A gas manifold controls the input gasses that do not need to be vaporized, H₂, He, Ar, NH₃. Separate ports allow the introduction of vaporized, volatile precursors such as TMS. Two pressure sensors monitor chamber pressure. A thermocouple gage is used to determine the quality of the vacuum produced by the mechanical pump, and a stainless steel diaphragm pressure gage is used to monitor the relative concentrations of the reactive gasses during their introduction. To decrease contamination the system is designed for temperature controlled multi-zone bake out. Waste and unconverted reaction gasses are diverted through a water trap neutralizer when the system is put under positive pressure. Dual mechanical pumps are used; one to pump the reaction chamber and one is used to pump the manifold between gas introduction stages.

The laser used in this study is an IPG Photonics 100 watt CW fiber laser with a 1070nm wavelength. A X-Y positioning stage supports mirrors and a focusing lens that direct the beam through the viewport. The focusing lens has an $f=150$ mm, and in the current configuration, produces a 100 μm spot size, established by test ablation of a tantalum film. A computer control system is used to control the laser output and beam positioning. A custom designed Labview code was written to control the deposition process. Laser modulation can be controlled by a waveform and power is calibrated to an external power meter. The X-Y stage is controlled so that individual layers are composed of a variable spacing raster pattern and each layer can have its own unique geometry. The deposition geometry and scan line spacing are also controlled by the code. Motion control is a

Proportional Integral Derivative feedback system, which controls servomotors with optical encoders

A flat titanium disk was used for surface deposits of Silicon Nitride. Scan rate, laser power, line spacing, geometrical design, and chemical composition were tested on this substrate. Another substrate consisted of a series of grooves machined into the disc surface with these grooves serving as a test bed for joint fill geometry. In order to evaluate the potential for powder infiltration deposits, the sample substrate used was a recessed dish filled with Si_3N_4 powder. Silicon Nitride joints were made by abutting two bevel-edged Si_3N_4 substrates both with powder fill and without.

Experimental Results

The SALD process has several parameters that must be evaluated to produce the best quality deposit. Laser power must be selected, so that decomposition can occur without uncontrolled run away growth. Scan speed must be considered in conjunction with laser power in order to get a consistent deposition rate. Initial tests were performed with a stationary beam to determine if growth is possible. Subsequent tests were performed at scan speeds ranging from 50 $\mu\text{m/s}$ to 1500 $\mu\text{m/s}$. Scan speeds faster than 1250, were poorly controlled by the servomotor resulting in a non-uniform deposition and poor adherence to the programmed geometry. 1000 $\mu\text{m/s}$ is the speed where the most uniform deposits are formed.

The laser power was varied for this experimental series. The laser used was capable of producing 10-100 watts of power. For this type of experiment, considering the small focal size, this is too much power. The laser was passed through a 70% reflection beam splitter with the excess diverted to a beam dump. The resulting laser power, 3-30 W, was sufficient for this series of experiments. Laser powers from 5-22.5 W were evaluated. It was found that 15 W produced the best deposit when used at a scan speed of 1000 $\mu\text{m/s}$. Decreasing scan speed necessitated a decrease in power. The deposition rate is extremely low below 5 W causing the necessary scan rate to approach zero. A scan rate of 50 $\mu\text{m/s}$ for instance, can have controlled growth at 9 W.

Additional parameters considered in these studies, include level of focus or defocus, and deposition pattern geometry. When making a SALD deposition the laser focus will change as the deposition builds. The higher the structure formed, the more out of focus the laser will be. The Rayleigh length of the laser and lens system used in these studies, defined by: $Z_R = (\pi w_o^2) / \lambda$ where w_o is the beam waist radius and λ is the wavelength is 7.3 mm. The defociuses used in this study were from 0.0 to -2.0 mm. It was possible to perform multiple layer depositions without refocusing as the deposit becomes thicker. In some test cases depositions as tall as 1 cm were grown from the substrate before the defocus was too great to support further growth.

The geometric configuration of the deposits was also varied. In many cases an arbitrary rectangular shape was chosen as the deposition pattern; however, when joining tests were performed the rectangle was defined by the plan view of the abutting beveled faces. The

raster patterns used were rectangular with alternating long and short sections. The length of the short sections defines the line spacing of the longer dimension. Line spacings of 2.5-50 microns were used in these deposition experiments. Line spacing of 50 μm introduced periodic voids into the deposition. Progressively closer spacing was used to minimize this and to decrease the presence of undesired phases. All joining was performed with a 2.5 micron line spacing. With the rectangular joint fill it is possible to make the raster in line with the joint axis or perpendicular to it. The deposition of multiple-layers was performed by rotating the orientation of subsequent layers by 90 degrees, creating a crosshatch pattern.

Characterization

After two and three dimensional deposition tests were performed for the purpose of optimizing the experimental parameters, simulation joint filling tests were performed. A titanium substrate was machined into a series of parallel triangular grooves. The grooves served as spaces that could be filled with deposited silicon nitride. Titanium was chosen because of its resistance to corrosion in the deposition atmosphere and its dissimilarity to the ceramic of study. Depositions were performed and the samples were cross-sectioned to indicate the extent of the SALD and SALDVI fill. Fig 25 is a SEM micrograph for the conditions described in the figure caption.

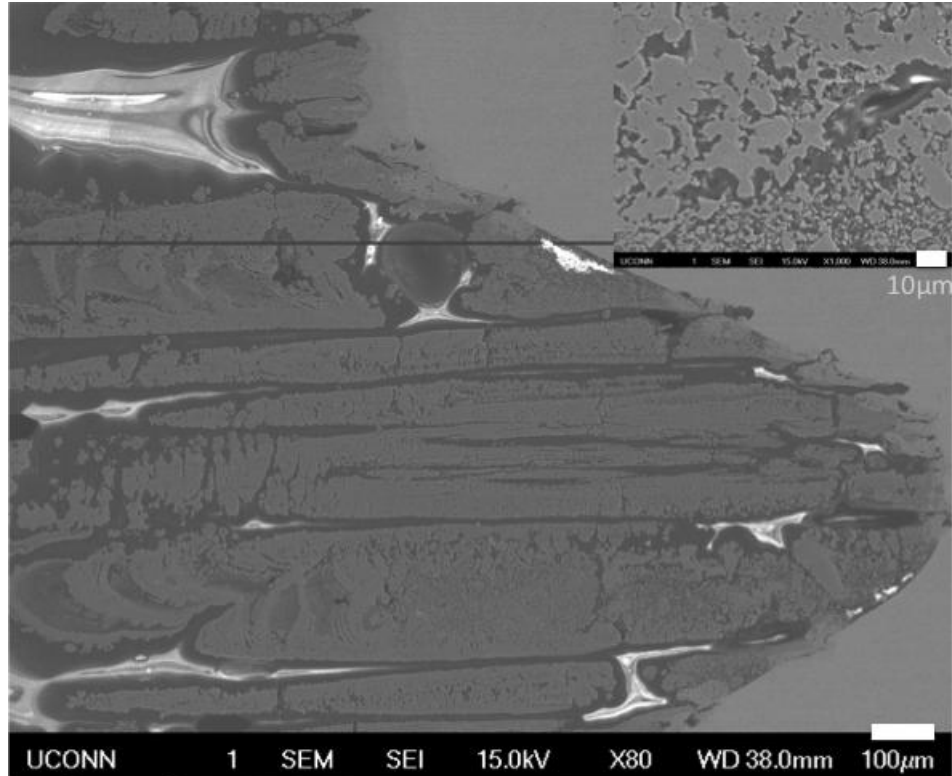


Figure: 25

SALD deposit filling a titanium substrate. The laser path from the perspective of this image is from the left to the right. The Experimental parameters were as follows: 15 W focused at the substrate surface with a scan speed of 1000 microns/s; TMS 17 torr, NH_3 45 torr, H_2 160 torr, He 160 torr; line spacing of 50 microns; and four layers of deposition. Image taken by a field emission SEM. The insert is a higher magnification figure taken from the deposit.

The groove fill deposition indicates the potential of the joining process. Cracks formed in the deposited material and some areas indicate porosity. Broad areas of the deposit do not have cracks or porosity and the interface did not show any delamination. A strong continuous interface is very important to the joining process where delamination could be a problem. The interface between the deposited material and the substrate is a chemical and mechanical bonding area. The laser power in this study is such that thermal decomposition occurs as well as substrate ablation. This results in an interface with a greater surface area and a mechanical keying effect.

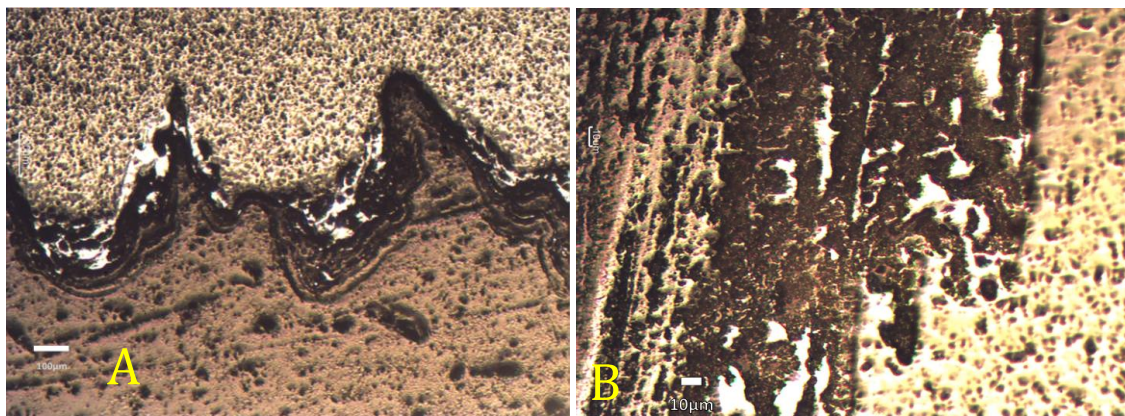


Figure: 26

a. Laser ablation and deposition with substrate above. b. Deposition into the beveled substrate, right.

The scanned laser creates microscopic grooves in the silicon nitride substrate through ablation when used as the substrate. The left image has a laser incidence direction from bottom to top. The image on the right was taken from a cross section of a joint. The light structure to the right is the substrate and the black and grey structure the deposition. The microstructure at the initial stage, A, is shown to be present in the initial phase of full growth of the deposited joint shown in B. Mechanical keying resulting from the laser/substrate interaction is seen on the beveled surface of the substrate.

The two best silicon nitride joints of this study shared the same gas phase conditions, 20 torr tetramethylsilane, 380-400 torr ammonia, 150 torr H_2 , and 150 torr He, which were

the optimal pressures. A laser power of 15 W and a spacing of 2.5 microns was used. One of the joints was performed under the SALDVI condition and the other under the SALD condition. The powder used for the vapor infiltration was also silicon nitride. Examples of the two joint are shown below:

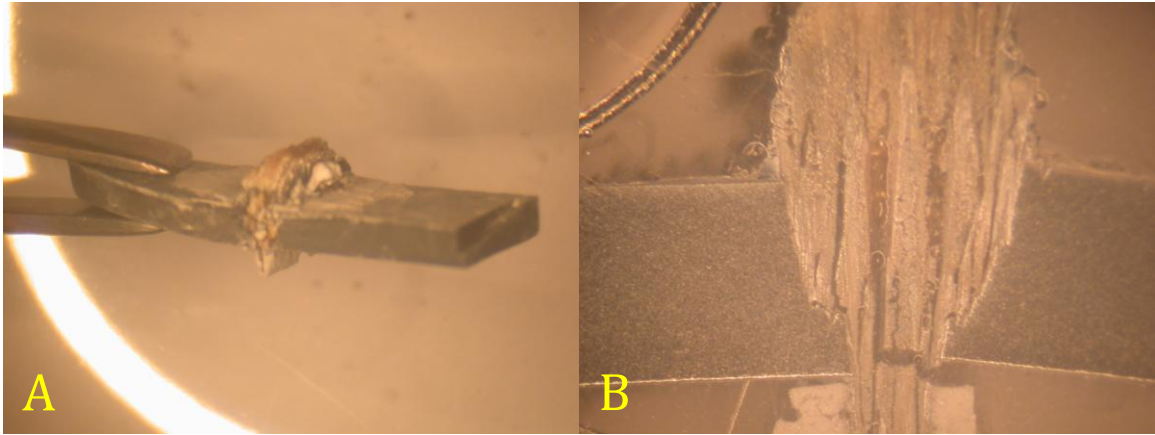


Figure: 27

Silicon nitride joints of silicon nitride substrates are shown. Image A above shows a perspective view of a silicon nitride joint where vapor infiltration was used. The substrates were resting on the surface of a powder dish, with powder loosely packed into the joint cavity. Image B is a cross section of the silicon nitride joint that did not utilize vapor infiltration. The work piece surfaces attached to the joint appear curved though were flat before deposition, the curvature is an effect of the laser ablation/deposition process. The excess material was not removed.

The silicon nitride SALDVI joint above had a lesser porosity and fewer cracks. Fracture of the joint did not occur at the interface indicating the relative strength of the bonding between substrate and deposition.

Chemical and crystallographic analysis indicates the presence of Silicon Nitride as a major phase in these joints. X-ray diffraction was performed on all deposition samples.

Below is an X-ray diffraction pattern corresponding to the deposition conditions above:

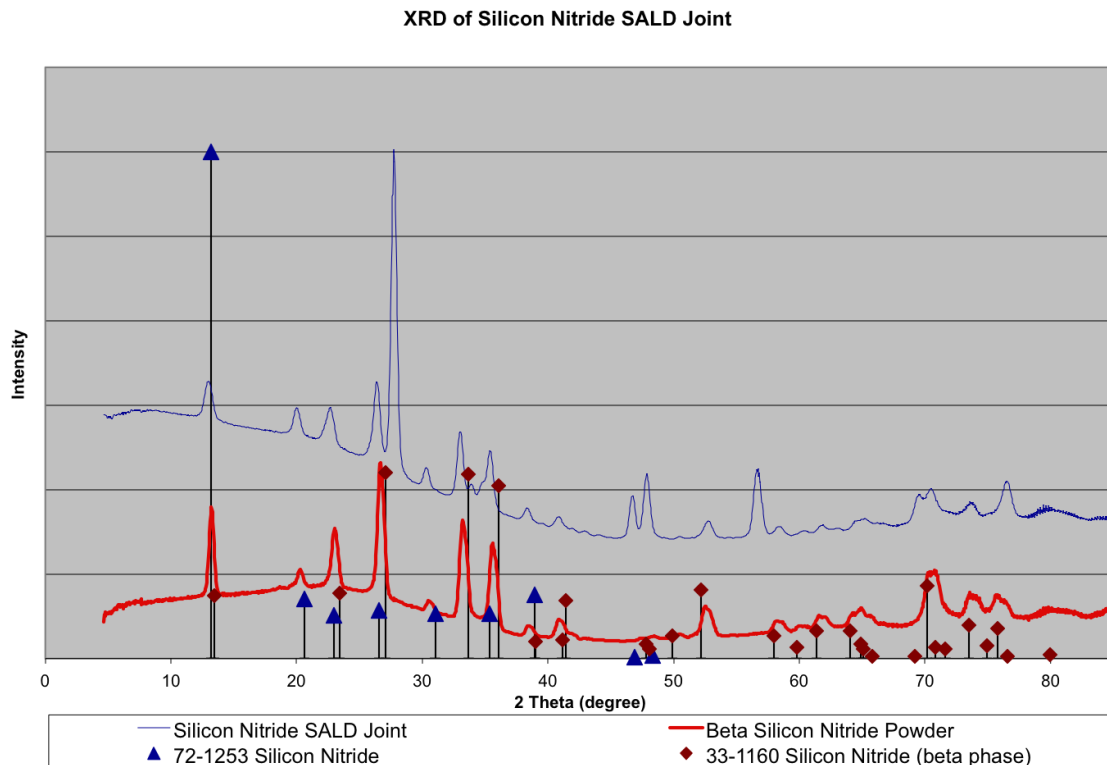


Figure: 28

X-ray diffraction pattern of deposited joint material compared to X-ray pattern cards and known Si_3N_4 beta phase powder indicating the deposit is primarily Si_3N_4 .

Conclusions

The joining of silicon nitride substrates with locally deposited silicon nitride is demonstrated. The SALD and SALDVI processes can create compositionally appropriate ceramic joints with good substrate/deposit cohesion, augmented by

mechanical keying. The process of localized chemical vapor deposition can be taken beyond the application the construction of arbitrary shapes. It is possible to join and consequently repair existing ceramic components. Joint density could be improved through further optimization of the experimental parameters but this type of joining is feasible.

Aluminum Oxide Precursor Evaluation

Certain potential precursors for the SALD process would have to be utilized at higher temperatures to achieve the desired deposition characteristics. The primary purpose for heating the system is to allow for increased vapor pressure of the reactants and consequently a higher potential deposition yield. Some of the precursors that have been explored will not be viable for this process if they are not heated. In general, the precursors would be heated to a certain temperature to achieve a desired equilibrium vapor pressure. The gasses would then be introduced to a chamber slightly hotter than the precursors partial pressure equilibrium temperature, so that condensation of the precursor gasses will be prevented within the deposition chamber. An example of a precursor that could benefit from an elevated temperature reaction chamber is Trimethylaluminum, for the aluminum source of alumina. An example of the vapor pressure verses temperature chart of Trimethylaluminum is shown below.

VAPOUR PRESSURE CURVE

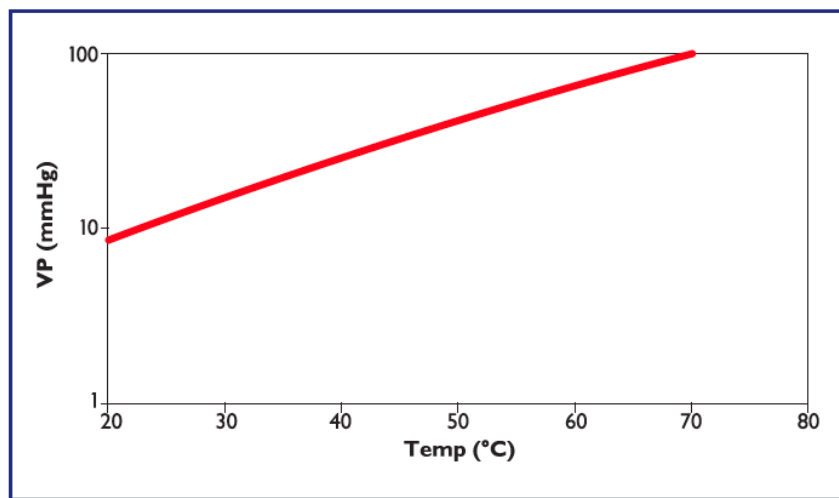


Figure: 29

Vapor Pressure Curve of Trimethylaluminum [45]: At ambient the vapor pressure is less than 10 torr, which limits the deposition rate. Elevating the system temperature will greatly increase the rate of precursor influx; a vapor pressure of 100 torr at ~ 70C would be suitable for deposition.

Trimethylaluminum, which could be used as a precursor for aluminum oxide, is a very difficult chemical to use because of its high reactivity. If used with TMA, an elevated temperature reaction chamber could greatly increase the available precursor and result in a faster deposition with a greater yield. Due to the high reactivity of TMA and the relative low reactivity of TMS it can be used as a test case for an elevated temperature system without the risk of contamination.

Al₂O₃ Precursor Evaluation for SALD Joining

SFF technology is not limited to the creation of components and objects. Freeform technology can be a mechanism for joining of materials. By defining the space between two objects as the boundary for a free-form object it is possible to form a three dimensional joint fill. Selective Area Laser Deposition or SALD, has been used for free form and joining of carbides and nitrides but has the potential to make other classes of ceramics. By selecting a metal-organic precursor and an oxidizer, an oxide can be created by CVD gas decomposition. In this study such oxide joint filler materials are studied, particularly alumina.

Gas phase laser chemical vapor deposition has been used for the formation of solid freeform objects. [57][24] The technology for Selective Area laser deposition or SALD and Selective area laser deposition and vapor infiltration, SALDVI can be modified for the purpose of joint formation and crack repair. In order to do this the crack or open space of the joint is defined as the inverse of a solid free form object and a computer scan path is generated for the laser. This technique has been used for the formation of silicon carbide joints of tubes in the SALD mode. [21] Joining attempts were made for flat plate specimens using the SALDVI method. [54][55][56] Silicon carbide and Silicon Nitride have been previously explored as the SALD joint fill material but oxides have not. Joining of aluminum oxide using SALD or SALDVI has not previously been reported.

Al_2O_3 deposited from the gas phase, is a material that is showing potential as a possible joint fill material, and precursors were evaluated for this type of deposition.

For formation of alumina, several solid precursors exist and have been used in the formation of films but their use necessitates heating for vaporization. They are then primarily used in flowing system hot or cold walled CVD reactors. [45][48] For deposition using an unheated chamber with a fixed gas supply, this type of precursor is not suitable. Trimethylaluminum, $(\text{CH}_3)_3\text{Al}$ was chosen as a source of aluminum because of its vapor pressure, 11 torr at room temperature; it is a liquid at room temperature. TMA has been used in several studies as the Al source for alumina in certain types of chemical vapor deposition, particularly epitaxial monolayer growth. Although this type of growth is not suitable for the SALDVI process, the experiments indicate alumina is formed with this chemical precursor. The studies also indicate several oxidizer choices. Oxygen sources that have been used for Al_2O_3 growth include, N_2O , NO_2 , H_2O and H_2O_2 . [19][26][37][47][48] Oxygen was not used in these studies because of the spontaneity of the reaction.

TMA is pyrophoric alkyl and will react immediately with atmospheric oxygen if released. This necessitates special handling and experimental restrictions. In order to use this chemical for deposition studies, the vapor is extracted into a vacuum and the liquid is never exposed to atmosphere or directly to any process oxygen. The TMA is used only below its room temperature vapor pressure to prevent condensation on the chamber walls

as a liquid. N₂O or H₂O were chosen as the first precursor possibilities. N₂O is a non-toxic gas that can be easily introduced at any pressure. H₂O was chosen because of its stoichiometric reaction potential:



Hydrogen is also added to this reaction though it is not stoichiometrically necessary.

Hydrogen in excess, as described earlier, assists in the formation of the desired CH₄ product instead of creating hydrocarbon contamination. [14]

The experimental setup for the formation of Al₂O₃ joint is a modified version of the SALD system. A manifold of gasses, Argon, H₂, N₂O and O₂ is attached to the system. The TMA and water are each uniquely valved off from the main system. The TMA feeds into a chamber that serves as a reservoir of vapor so that the TMA liquid does not contact the process gasses. There is a similar chamber for water vapor to prevent the TMA vapor from coming in contact with the liquid water. When introducing the precursors into the system it is desirable to introduce them in the vapor form. The sample work stage is within a vacuum chamber with a window for the introduction of the laser beam. The laser is moved externally by a computer controlled X-Y stage. The laser used in this study is a 1070 nm wavelength fiber laser that is CW up to 100 watts. The laser is operated with a 70% beam planar beam splitter, as there is instability below 10 watts. With the filter the laser is precisely controllable between 3 and 30 watts. The laser power and stage motion are controlled with a custom National Instruments Labview Code. This code is capable of interpolating a three-dimensional machine path, either directly imputed or from a CAD file. The experimental setup is shown in figure 30.

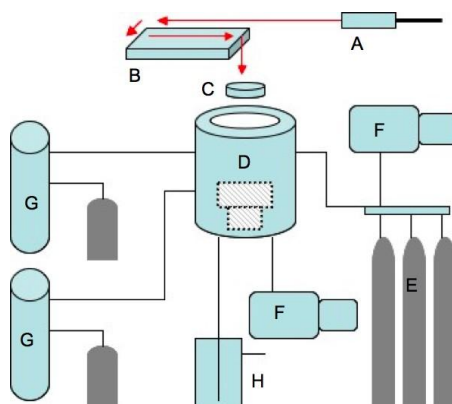


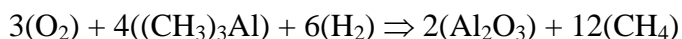
Figure: 30

Schematic of Deposition and Joining Setup. A) Fiber laser 1070 nm B) X-Y Stage with optical train C) Focusing Lens D) Reaction Chamber E) Gas Cylinders and Manifold F) Vacuum Pumps G) Liquid Precursor and Expansion Chamber H) Chemical Neutralizing Bubbler

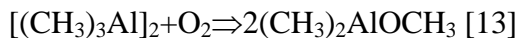
The experimental procedure for the determination of viable precursors is as follows. The reaction chamber and expansion chambers are flushed with argon and evacuated multiple times and a 50 mtorr or lower vacuum is established. The reaction chamber and one expansion chamber are filled with TMA vapor and then evacuated to one torr below vapor pressure, vapor pressure being approximately 11 Torr. If water is to be used as the oxidizer the second expansion chamber is filled with water vapor. The partial pressures within the expansion chambers are regulated to achieve the correct ratios upon mixing. Expansion chambers are used so that no liquid, H_2O , H_2O_2 , or TMA, can come in contact with a gas with which it might react. The liquids are thus mixed only in the gas phase. Once these precursors are mixed in the gas phase, additional process gasses are added.

The gasses, which may be introduced into the current set up, include: hydrogen, argon, nitrous oxide, oxygen, and ammonia. Each gas is introduced through a manifold that has been evacuated so that each gas quantity is controlled.

The purpose of these studies is to ascertain an oxidizer and aluminum source that can be used for pyrolytic laser CVD. A deposition is desired that will match the substrate composition, achieve a high degree of density, and show good adhesive properties to the substrate. Oxygen is not listed as a potential precursor to be used with TMA, since it reacts spontaneously. In order to test oxygen as a potential precursor, two torr O₂ was introduced into a chamber with TMA at vapor pressure. Low oxygen partial pressure was tested for the purpose of finding a lower limit below which, a spontaneous reaction would be prevented or slowed to a negligible pace. Even at this low partial pressure the O₂ rapidly reacted without any heat input from the laser. Below 2 torr the theoretical yield of Al₂O₃ would be too low. The reaction:



was expected but since the reaction proceeded without the hydrogen addition, another reaction is likely. A fine alumina powder, which stayed suspended in the air for several minutes, was created by this reaction as well as potentially other byproducts. Studies indicate the reaction:



as also likely.

Water vapor and N_2O have both been used as oxidizer sources with TMA. Water vapor and TMA will react to form amorphous Alumina, tested by EDS and X-ray diffraction, if the reaction occurs as a liquid based reaction. This was tested by using an over pressure of H_2O and TMA, achieved by heating both liquids so that their vapor pressures would be doubled and allowing this super saturation to mix as a gas. The resulting reaction occurred both within the gas phase and on the surface of the reaction chamber, depositing Al_2O_3 on all cold surfaces and constriction points. When the water and TMA were maintained 1 torr below their vapor pressures the spontaneous reaction either did not proceed or proceeded at a very slow rate.

Nitrous oxide did not react spontaneously with the TMA at room temperature at any partial pressure of N_2O . Gas combinations of TMA, hydrogen and a single oxidizer source, either N_2O or H_2O did not yield a controlled deposition. By combining N_2O and H_2O with hydrogen, argon, and TMA, both SALD and SALDVI deposits were then possible.

Using TMA as the aluminum source, and the combined oxidizer phase of H_2O and N_2O , alumina deposits were formed, both as a deposition into a powder bed and a deposition onto a substrate both alumina. The SALDVI deposition occurred within an alumina powder bed. The bed was created by repeated powder placement, agitation, and flattening by metal scraper. The powder surface was placed at the focal distance of the primary lens. A laser power of 15 watts, CW, was used to create a 3 mm square raster

pattern with 50-micron spacing between raster lines. The focused spot diameter at the powder surface was 100 micron. The laser scan speed was 25 microns/s. The TMA and water vapor were used slightly below their vapor pressures. Argon, Hydrogen and N₂O were all added at 150 torr. EDS performed on these deposits confirms aluminum and oxygen ratios of matrix and powder regions of deposit that closely approximate Al₂O₃. X-ray diffraction indicates alumina. The resulting deposition is seen below in the ESEM micrograph, Figure 31:

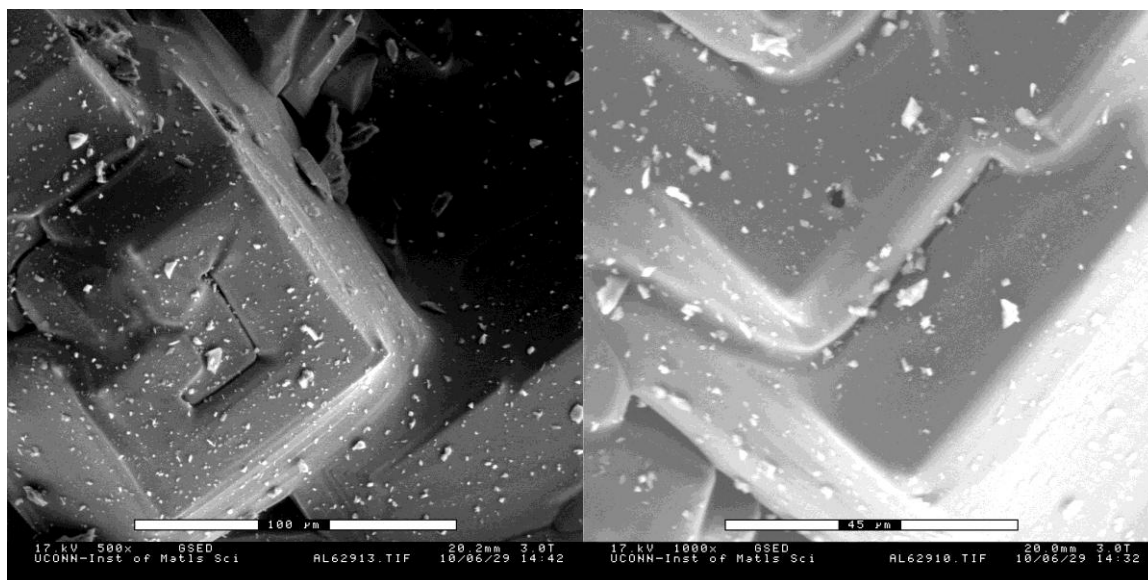


Figure: 31

500x and 1000x ESEM micrographs of SALDVI deposition of alumina into an alumina powder bed. Note the particles imbedded within the deposited matrix.

The SALDVI deposit above appeared dense and was approximately the expected deposition geometry.

Deposition of the SALD type was also performed onto an alumina substrate. The conditions for deposition were the same as above except the raster pattern defined a 1 cm x 2 mm scan area and the laser passed each spot 6 passes as apposed to four of powder bed deposition. A deposition was formed with a crisp interface as seen below in figure 32:

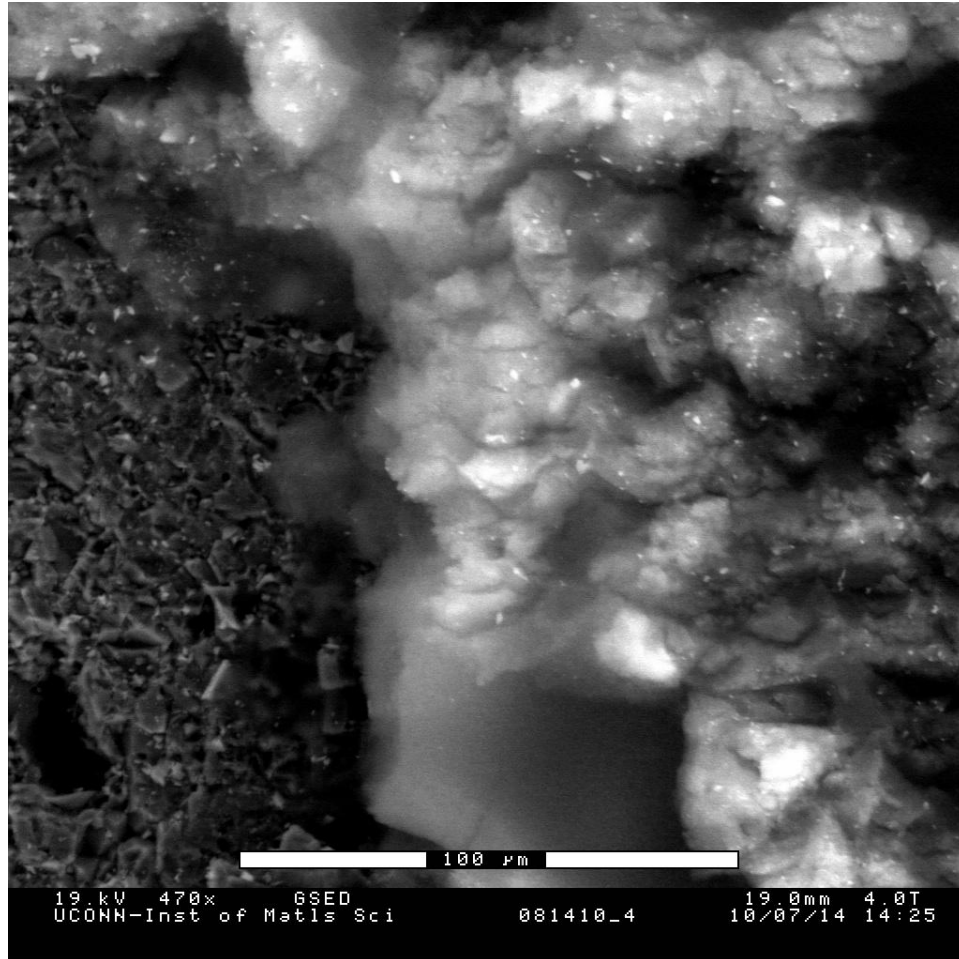


Figure: 32

SALD type deposition of alumina (right) on a sintered alumina substrate (left) at 470X magnification

The deposition was a distinctly different from the substrate but failed to achieve the desired density. The deposition did show very good adhesion to the substrate. X-ray diffraction patterns of the above substrate and deposition are shown below in figure 4 as well as an alumina pattern, which closely matches both materials.

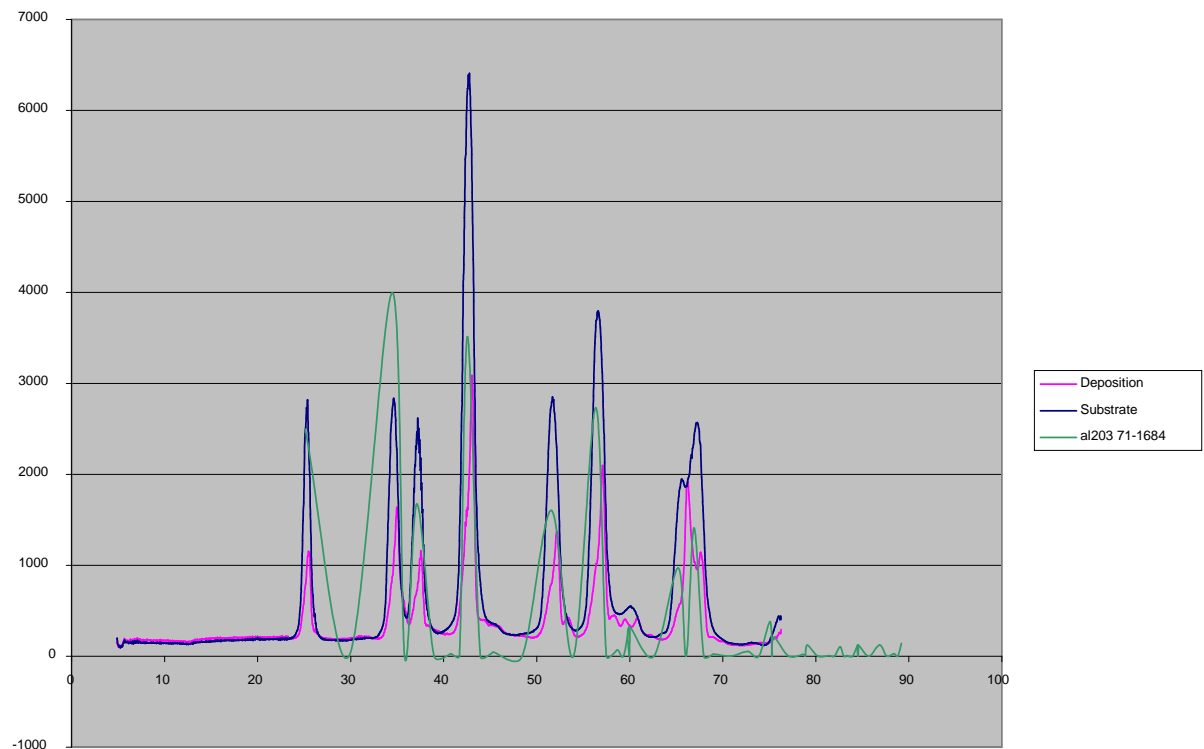


Figure: 33

X-ray diffraction patterns of substrate, deposition and corresponding pattern from card 71-1684 alumina.

In an initial SALDVI joint attempt was performed that resulted in a deposition into powder and adhesion to one work piece face. The deposition was composed of only two laser raster passes and consequently resulted in a non-dense deposit. Seen below in figure 34 is a deposit on a joint wall.

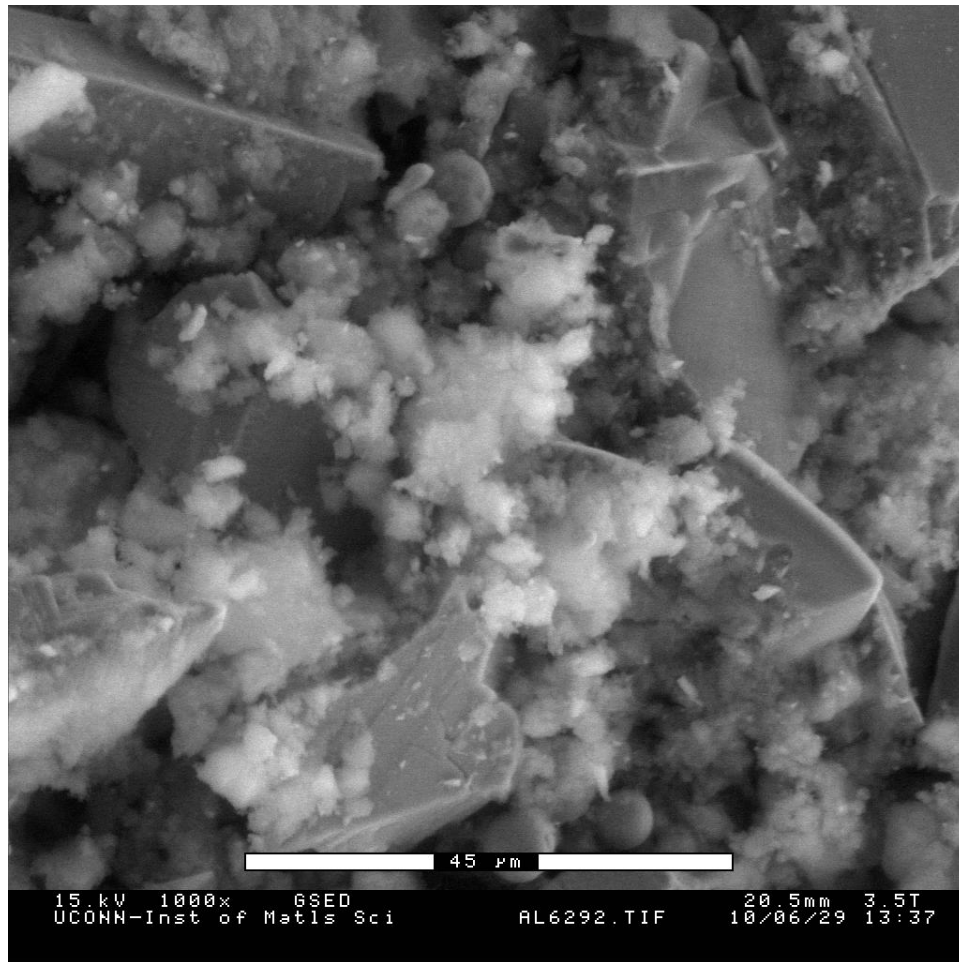


Figure: 34

ESEM micrograph of SALDVI type deposit joint fill material. The light fluffy region comprises the deposited material and the larger crystalline shards are powder that has been infiltrated. The base substrate is not seen in this image.

Alumina Deposits were successfully made by combining the precursors of trimethylaluminum, nitrous oxide, hydrogen and water vapor. It was possible to use a computer defined laser path to make a deposit of the same geometry. The deposits were well adhered to the substrates. Shorter laser exposure time, resulting from fewer laser

passes, resulted in deposits that were not dense. The density and adhesion increased with increasing laser dwell time.

As a precursor for the aluminum component, TMA has potential. A combination of H_2O and N_2O serves as an oxygen source; however, the exact nature of the reaction is not known. There are difficulties in densification and localization of the reaction to the substrate or powder surface; compositionally the alumina is as desired. If these conditions are improved, then joining will be possible with the SALDVI technique for alumina substrates.

Selective Area Laser Deposition Joining of Aluminum Oxide

Selective area laser deposition (SALD) is a chemical vapor deposition technique used to deposit ceramic material. The technique allows localized deposition in the area of the laser spot; complex depositions can be achieved through the use of a computer control program. It is possible to free form fabricate arbitrary shapes. In particular by defining the space between two work pieces as the envelope for deposition, it is possible to form a monolithic joint. The use of a trimethylaluminum and diethyl ether precursor system is explored as a means of depositing aluminum oxide. The alumina is used as joint fill material for alumina SALD joining.

Introduction

Selective area laser deposition (SALD) is a type of localized chemical vapor deposition where the driving force for deposition comes from the heat of a laser spot. The process is pyrolytic, decomposing gas phase precursors to form solid deposits where the laser has heated a substrate. The process is computer controlled; laser power, spot position and velocity can be controlled. Arbitrary deposition patterns can be created allowing the process to be used as a means of solid freeform fabrication of ceramic materials. [8] If the shape of the deposit is programmed to be the negative space between two work pieces, it is possible to form a joint between two substrates through additive manufacturing means. In a process analogous to welding two work pieces are joined with a filler material of the same chemical composition. Unlike welding, the fill material is deposited in-situ as a byproduct of a chemical reaction in the joint space, as apposed to being derived from melted external stock. This allows materials to be joined that have extremely high melting temperatures or that do not form a liquid phase. The solid freeform technique Selective Area Laser Deposition (SALD) has been used as a means of joining ceramic work pieces with a monolithic and chemically homogenous ceramic fill material. Silicon carbide and Silicon nitride have been described earlier. The deposition of an oxide material further demonstrates the versatility of the process.

In order to deposit an oxide material such as aluminum oxide (Al_2O_3) it is first necessary to establish a viable precursor. The SALD process uses volatile liquids of gaseous precursors that are the source of the constituent elements of the ceramic deposit. For the

case of alumina, sources of both aluminum and oxygen are necessary. As a chemical vapor deposition process, the SALD precursors have similar requirements to those used in conventional CVD, volatility, gas state stability and the potential for controlled decomposition. As the SALD process is a laser driven process, the decomposition reaction environment can be more hostile. High temperature gradients can exist between the laser-induced thermal zone and the surrounding ambient temperature substrates. The laser interaction with the substrate also serves to create a reactive plasma. Since there is a high, localized, temperature and reactive plasma the reaction rate can occur more rapidly than conventional CVD if there is a high enough reactant flux into the reaction zone. A SALD precursor must have a high enough vapor pressure to create bulk deposits on a feasible time scale.

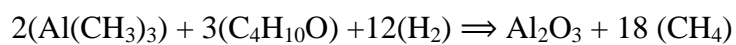
Metal organic precursors, specifically aluminum alkyls such as trimethylaluminum or TMA, $\text{Al}(\text{CH}_3)_3$ are potential precursors. TMA is a volatile aluminum source that has been used as an aluminum source both for pure Al deposits and as the aluminum constituent of Al_2O_3 . [6] TMA is a similar metal bearing alkyl to tetramethylsilane TMS, $\text{Si}(\text{CH}_3)_4$, which has been used with success for the SALD deposition of silicon carbide and other such compounds are frequently used in other CVD systems.[40] TMA is pyrophoric and highly reactive with a variety of oxygen sources so special handling apparatus' are necessary as well as a carefully chosen oxygen source.

Alumina deposition with TMA requires an oxygen source. TMA is highly reactive with O_2 , and will react in the gas phase. Water vapor and hydrogen peroxide vapor have been

used as oxygen sources for alumina but are too reactive for SALD type deposits, as previous studies have shown. [26][47][48][54] Low concentrations of the oxidizing gas could be used to form small amounts of alumina but the resulting reaction is too low yield for the SALD process and increased gas concentration results in spontaneous decomposition.

In order to find a precursor that would not cause spontaneous decomposition in the gas phase, different sources of oxygen were explored. There are organic gasses that are volatile, contain oxygen and have potentially high vapor pressures. Ethers contain oxygen centrally bonded to two alkyl or aryl groups. These chemicals are highly volatile and are stable in their gaseous state. Ethers have been used as oxygen sources for CVD reactions with metal organic gasses and have not resulted in spontaneous decomposition. [22][31][40] Ethers have the additional characteristic in the gas phase of potentially forming gas phase complexes with metal organic gasses. [31] Due to the availability and high vapor pressure of diethyl ether, it was chosen over a variety of other ethers and tert-butyl ethers for this study. Diethyl ether has a vapor pressure of 400 torr at room temperature. This vapor pressure is higher than necessary for the SALD process.

To make alumina Diethyl ether, $C_4H_{10}O$ and TMA, which can occur both singly and as a dimer [], were chosen as the active precursors. A stoichiometrically-balanced equation for a potential decomposition reaction is shown below:



Hydrogen is added to provide the full conversion of the C and H to gaseous methane.

[14][30] This formula was the basis of the gas composition used for the deposition experiments.

The procedure normally followed for the SALD deposition had to be somewhat modified for the above precursor combination. The vacuum chamber used for the deposition experiments is evacuated and back filled with argon or helium 5 times and the whole system is pumped down to <100 mtorr. From this evacuated state, the chamber is filled with the reactive gasses, then inert gas, and the total pressure is kept as a partial vacuum. The gasses are introduced into the reaction chamber and the total chamber pressure is monitored by a diaphragm vacuum gauge. This pressure can normally be read as directly correlating with total gas quantity. This is a good measure of the added gas quantities as long as the gas does not react in the gas phase. The combination TMA and ether into a clean and evacuated reaction chamber does not result in spontaneous decomposition, which would be indicated by the formation of alumina powder appearing as white smoke. Instead, a pressure change is observed with no apparent decomposition. TMA has an equilibrium vapor pressure of 8.6 torr at 20 C found from the equation; $\text{Log } P(\text{mmHg}) = 8.22 - 2134.8/T(\text{K})$ [44][45]. In the deposition process it is important to prevent the pressure from exceeding this point within the vacuum chamber because condensation will occur on the chamber walls. When 6 torr of TMA is added to the reaction chamber first, then ether is slowly added, there is an observed pressure drop to 3 torr at which point the pressure begins to rise. The effect is repeatable and potentially indicates the

formation of a gas phase complex of the two reactants. The effect is observed when the first gas introduced is ether and the second gas is TMA. In this case a pressure drop is observed but without subsequent pressure increase and eventual visible condensation on the reaction window. The gas mixture is then used as a source of both aluminum and oxygen during the decomposition process.

The experimental deposition system is set up to perform SALD depositions. The system consists of a Labview computer control program that controls the power of the laser and the motion of an X-Y optics positioning stage. The optical train positions the beam above the desired section of substrate and a focusing lens converges the beam. The laser enters into the reaction chamber through a viewport and the focused beam hits the substrate and substrate holder. The substrates for these alumina depositions are titanium disks, alumina disks, and alumina beveled work pieces. The titanium disk is used as a deposition substrate so that the purity of the alumina can be confirmed independent of an alumina substrate. Alumina disk substrates were used to show the adherence of the deposited material to a like substrate. The flat beveled substrates were used to demonstrate the potential for joining alumina to alumina with an alumina joint fill.

Experimental Materials and Methods

The deposition and joining experiments were designed to test a variety of experimental conditions. Each deposition uses a combination of laser power, scan speed, and spot size to create a localized heat zone that drives the decomposition reaction. The chemical

composition the gas precursor mixture is also varied. The deposition pattern is varied with respect to the final desired shape, in the case of joining; the deposition pattern is customized according to the joint width and length.

Laser power variations include: 10, 15, 20, 30, 35, 45, 60 and 70 W. Depositions that occurred above 45 W were too energetic for controllable depositions and resulted in runaway growth, gas phase decomposition, and window contamination. The scan speed variations include: 10, 15, 30, 45, 50, 90, 100, 150, 175, 360 micron/s. The scan speeds of ≤ 15 resulted in excess heating of the viewport resulting in contamination through decomposition or partial decomposition. Scan speeds above 170 $\mu\text{m/s}$ resulted in uneven decomposition and would require excessively high laser power. Laser spot size was fixed at 150 microns achieved through a combination of fixed focal length lens, and a defocus of 10 mm below the work piece surface.

The precursors used in the deposition experiments are TMA, diethyl ether, H_2 and inert argon. Due to the previously described pressure reduction effect it is not possible to fully define the ratio of TMA to ether. A method was devised for introducing these gasses into the vacuum chamber. TMA or ether is introduced first to one quarter the desired final pressure the other gas is then introduced allowing the pressure to drop then equalize. This process is repeated 4 times and the mixed gasses are brought to the desired pressure. In this way a slow gas phase mixing was allowed and the gas phase reaction remained stable. If the first gas introduced is TMA the mixing is terminated below the 8 torr mark. Additional ether can be added beyond this point to increase the availability of oxygen in

the system. If the ether is added first the pressure can be incremented to 24 torr for the mixed gas final pressure. Beyond this point TMA addition does not increase the total pressure without resulting in condensation. Additional Hydrogen is added to the system in 25, 80, 96, 100, 120 and 200 torr quantities. And the concentrations of Ar used are 50, 80, 100, 120, 192 torr.

The deposition pattern used for joining purposes was designed for maximum coverage of the joint area with the laser spot. Instead of a square raster, of the type used in previous studies, a circular over lapping raster was chosen.

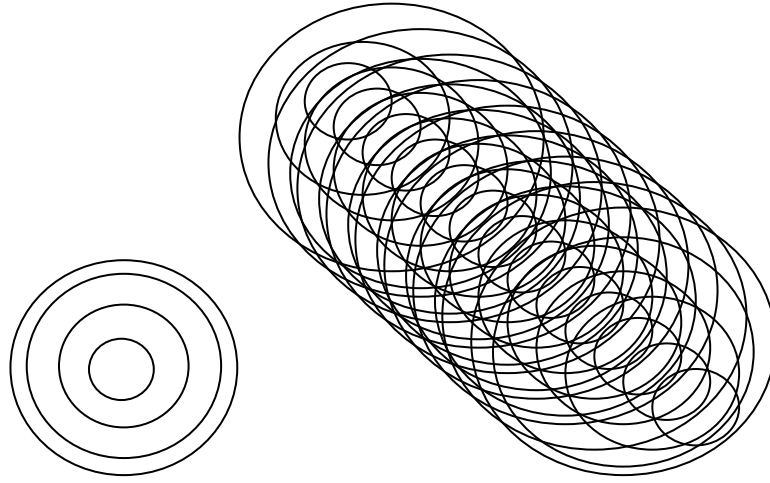


Figure: 35

The laser raster pattern is defined as 4 concentric circles translated along the joint axis in a series of overlapping paths.

Joining experiments were performed on solid substrates with two beveled work pieces nearly abutting off set from the substrate below by carbon tape. The carbon tape affixed the work pieces during the joining process and allowed a small gap for reactive gasses to diffuse to the underside of the joint during deposition.

Experimental Results

Al_2O_3 deposits were made with the objective of joining two alumina substrates with an alumina joint fill. Utilizing a chemical precursor combination of TMA, ether, H_2 and Ar, samples were tested with an aim of showing that alumina can be a deposition product. A typical, representative deposition was performed under the following conditions: TMA

was introduced into an evacuated reaction chamber. 2 torr of TMA was added, then 2 torr of ether. The process was repeated until the total pressure remained stable after the last addition of TMA. An ether over pressure was added bringing the pressure from 30 torr to 58 torr. 96 torr of H₂ was added. The scan speed was 30 microns/s with a laser power of 15 W. A SEM analysis of the deposit is shown below:

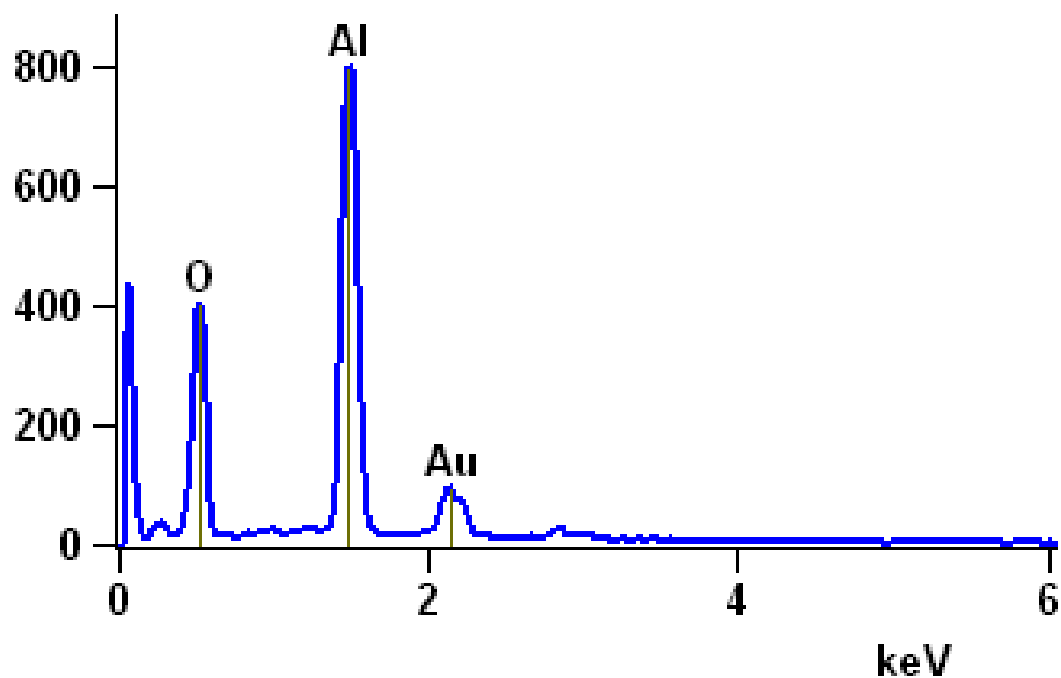
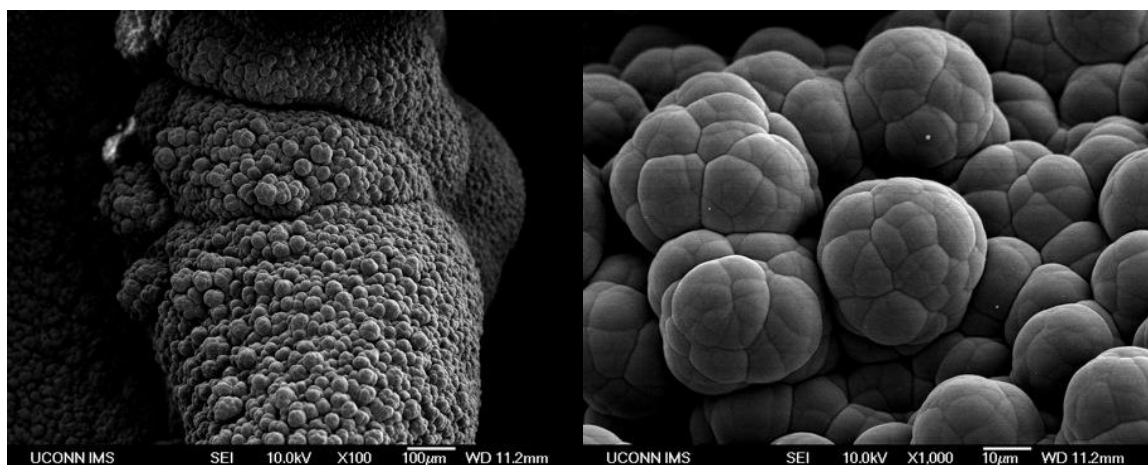


Figure: 36

The surface morphology of an alumina deposition test deposit is shown at two magnifications. The deposited material is polycrystalline, with several smaller grains coalescing to round grain clusters these clusters then forming a dense bulk structure. Shown below is EDS elemental analysis of an area approximately 50

microns across, which indicates the elemental constituents of oxygen and aluminum. Gold spectrum indicates the presence of a conductive sputter coating.

EDS chemical analysis indicates a 42 atomic percent Al, and 55 atomic percent Oxygen, which would be 40 and 60 % in the stoichiometric case.

Pure alumina is white and the deposited material resulting from the TMA-ether chemistry has a grey to black color. The black color most probably indicates a carbon contamination in the alumina; however, this carbon does not exist, as a measurable second phase so is likely a lattice scale defect or part of an amorphous constituent.

To test the theory of carbon contamination in the crystal lattice a sample joint was placed in a furnace for two days at 1000 C. It was predicted that the black deposit would turn white after the carbon had a chance to diffuse out.



Figure: 37

A joint fill was deposited between two beveled and abutting pieces of aluminum oxide. The joint material deposited was black during the experiment. A heat treatment was performed and the deposited material turned white. No macro scale volumetric or size change was observed.

X-ray diffraction was performed before and after the heat treatment, shown below:

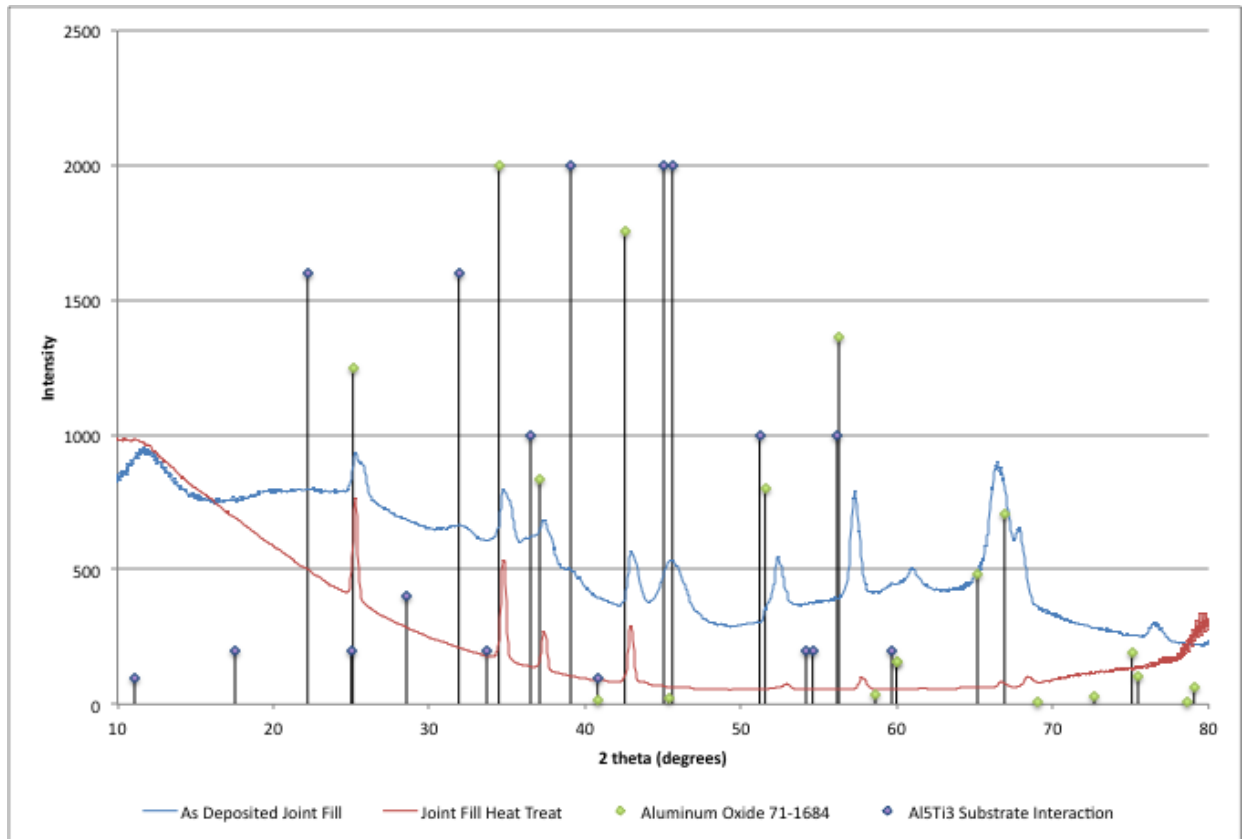


Figure: 38

X-ray diffraction pattern indicating the crystal structure of pre and post heat treatment joint fill material. The above pattern indicates the material as deposited. Alumina composition is confirmed with the presence of an amorphous phase. There is a second phase that is an accidental byproduct of the substrate (Ti disk) and the TMA interaction. After the burn out and incidental heat treatment the resulting material still corresponds with Alumina with a reduction in the amorphous component. High angle peak shifts in both cases, indicates the presence of a lattice-distorting defect. The presence of hydrogen or carbon in the crystal structure could account for this shift.

The joining of ceramic work pieces with chemically homogenous filler is accomplished if several conditions are met. The deposited material must be of the same chemical composition of the ceramic work pieces. The deposited material must be dense and free from pores. The deposited material must bond to each work piece and fill the joint space. The specific geometry used for the joining tests makes full penetration to the base of the joint also a requirement.

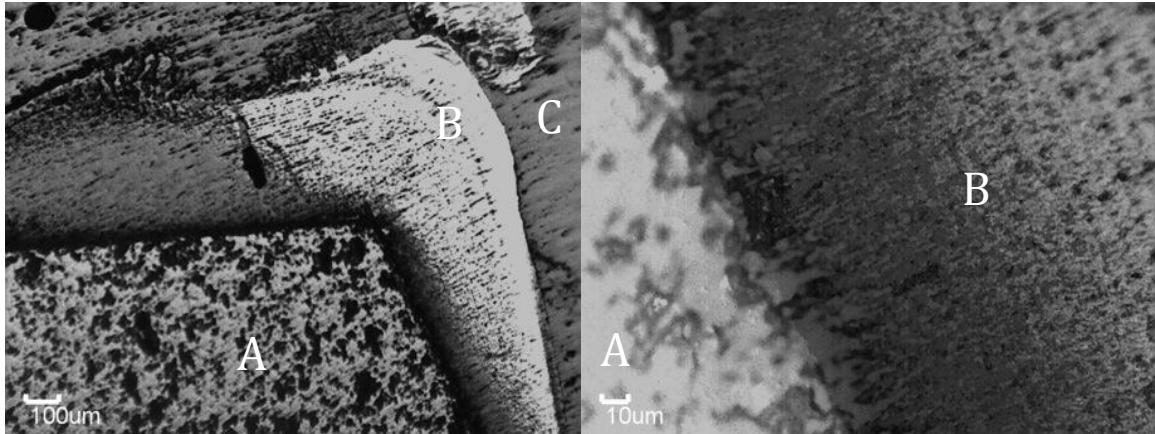


Figure: 39

The condition of adhesion between substrate and deposited material is shown.

The left image shows the interface between material deposited at the top of a beveled joint and the substrate. A magnified image, right, indicates a pore free interface where the substrate is on the left and the deposited material is on the right. Grains of deposited material of the same order of magnitude as the substrate are seen growing from the substrate surface. Smaller grains are seen in the bulk deposit approximately 25 microns from the surface of the substrate. In all figures, A indicates the alumina substrate, B indicates laser deposited alumina, and C indicates mounting compound.

The geometry of the joint and the growth mechanisms of the deposited material resulted in difficulty achieving full joint penetration, and wall adhesion.

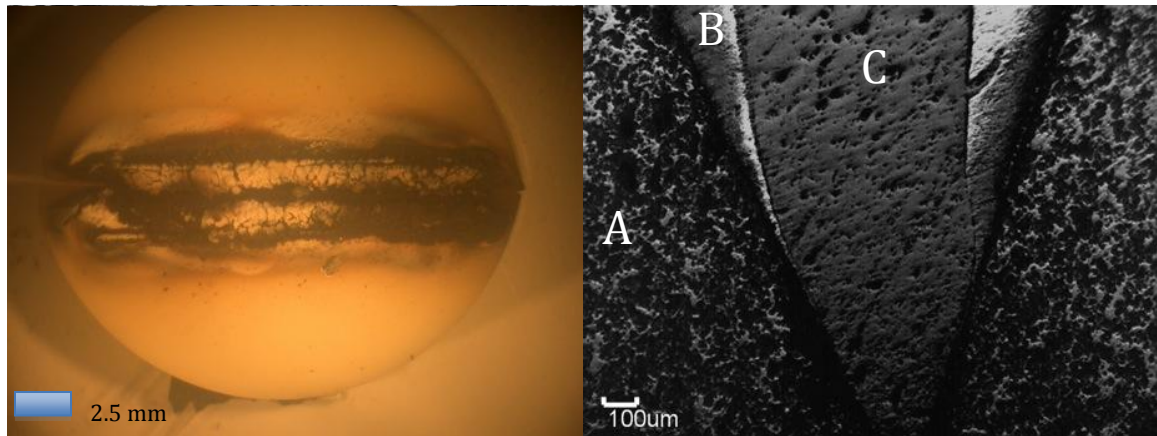


Figure: 40

A joint between two alumina semicircular disks with beveled edges is shown in the left micrograph. Growth has occurred from each work piece face. The deposited material grew toward the center but ultimately resulted in the closing off of the beam pathway. The partial penetration into the base of the joining work piece is shown to the right.

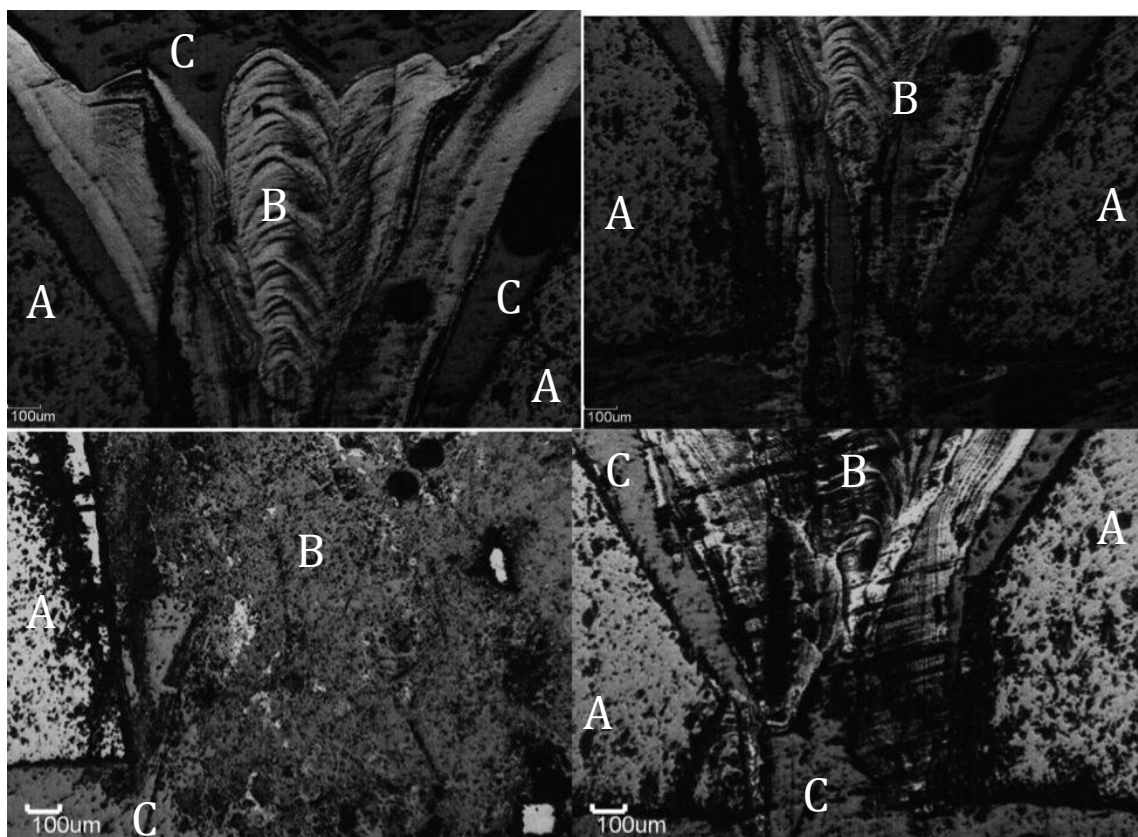


Figure: 41

The micrographs above indicate a joint between two alumina substrates joined with an alumina deposit. The top two micrographs represent the top and bottom of the joint at low magnification. A relatively full joint is observed with low porosity. The joint does suffer from delamination from the substrate walls potentially due to a thermal mismatch between the substrate and the bulk deposit. Shown below are examples of the deposition fill at the base of a joint. The left image indicates a deposit fully penetrating the joint. The right micrograph indicates full penetration with partial delamination.

Conclusion

The SALD process shows potential for joining ceramic oxides by using aluminum oxide as a test case. A precursor that consistently yields alumina on decomposition was chosen and chemical and crystal structure analyses were performed of the deposition product. Joints were formed between alumina substrates with an alumina joint fill. The quality of the deposit and the interface were examined. Deposits that initially appeared black as deposited were converted to a pure white alumina without large volumetric or porosity changes. Though the process could be improved, SALD has potential for joining of oxides and other classes of ceramic material if the correct precursors and experimental conditions are chosen.

Future Modifications to Enhance Process

The SALD deposits are performed with the process gas introduced as a batch. The process converts the process gas into ceramic deposits and waste gas. The concentration of process gas decreases and the presence of waste hydrocarbon gas increases. If the batch is not refreshed periodically the deposition can become contaminated from the waste gas presence. A flowing system, which would use more precursor volume, would reduce the presence of waste gasses in the reaction zone. A flowing system would, however, be a more complex system that would require mass flow controllers, a reaction chamber designed for laminar flow, and an exhaust system designed to neutralize the process gasses while maintaining the correct chamber pressure.

Many of the deposits, across various precursor compositions show evidence of undesirable, amorphous contamination. This contamination is most probably the result of incomplete decomposition of the precursors. It is proposed that this contamination could be reduced through system design modification. The laser power intensity profile is a Gaussian shape that is averaged to give the lasers nominal power. The intensity is highest in the center and decreases as the perimeter is approached. This power profile results in non-uniform heating across a laser spot. If the collimated beam were exposed to a mask, which removed the weakest part of the laser power profile a more uniform deposit, might result. A second method that could be employed is the use of a laser for the purpose of cleaning the work piece between layer deposits. This would necessitate the evacuation of process gasses after the deposition of a SALD or SALDVI layer, and a laser scan across the previously deposited material. A laser pass could vaporize the

contamination on the layer surface, preparing the surface for subsequent layer deposits. After a clean up pass, the chamber would be refilled with process gasses. This would be a time consuming addition to the deposition process but it might result in cleaner deposits with good interlayer cohesion.

The use of a pulsed laser creates a surface texture on the ceramic substrate, which can assist, in the joining process by creating a mechanical keying effect. The pulse laser deposits material onto and ablates material off of the surface. While there is a net growth, the overall deposition rate is decreased. If a system was designed that incorporated two lasers, a pulsed and a CW laser, it would be possible to use the mechanical keying effect in conjunction with more controlled deposition. This effect could potentially be achieved with an additional axis of motion control, connected to the focusing lens, along the Z-axis. By focusing at the substrate surface for ablation steps and defocusing for deposition steps it would be possible to use the best aspects of both conditions.

The highly volatile TMA was successfully used for joint formation but in many cases the chamber contamination was very severe. This limits the usefulness of the manufacturing technique. While other precursors could be explored, a modification of the ether and TMA precursor system could yield more manageable results. Since the TMA seem to form a complex in the gas phase that does not spontaneously decompose, it would be worth exploring if this complex could be formed in the liquid phase. If a liquid phase complex of TMA and Ether were stable it could be used as a single source precursor for the deposition of alumina. Other chemical systems should also be investigated

The SALDVI can be effective in the formation of ceramic joints. Each test run of this process was performed by manually placing the powder in the joint before layer deposition. If joining studies in this area were extended it would be necessary to develop a system of in situ powder delivery that would deliver powder directly to the joint space. This would bring the joining process closer to commercial viability as more automation is incorporated.

Conclusions

The technical challenge of joining ceramic materials inspired a new approach. SALD and SALDVI techniques that have been used primarily as free form manufacturing techniques were modified to form monolithic ceramic joints. The SALD and SALDVI processes have been studied. The deposition techniques have been used in the creation of silicon carbide, silicon nitride and aluminum oxide; these ceramics being technically relevant examples of their respective classes. Precursor chemistries have been explored for SiC, Si₃N₄, and Al₂O₃

This work shows several novel contributions to the field of additive manufacturing. A deposition apparatus was built that can be used for SALD and SALDVI depositions with varying degrees of complexity and compositions. SiC-SiC joints were formed with the SALDVI technique. The joints were an arbitrary size, which was possible through the use of a control program of flexible design, which can be adapted to many experimental

configurations. Silicon nitride joints were performed in a similar way, extending the SALD and SALDVI process to the joining of nitride ceramics. The evaluation of aluminum oxide precursors yielded an effective precursor composition, which could be used in a CVD process independent of the SALD mode of operation. The precursor was successfully used to create alumina joints with an alumina fill. The flexibility of the SALD and SALDVI processes was demonstrated through the formation of silicon carbide, silicon nitride, and aluminum oxide, freeform joints.

References

- [1] A. Ahmed, E. Siores, Microwave joining of 48% alumina-32% zirconia- 20% silica ceramics, *Journal of Materials Processing Technology* 118, 2001, 88-95
- [2] O.M. Akselsen, Review, Advances in brazing of ceramics, *Journal of Materials Science* 27, 1992, pp. 1989-2000
- [3] S.D. Allen, Laser chemical vapor deposition: A technique for selective area deposition, *Journal of Applied Physics*, Volume: 52, Issue:11, 1981, 6501-6505
- [4] S. Aravindan, R. Krishnamurthy, Joining of ceramic composites by microwave heating, *Materials Letters* 38, 1999, pp. 245-249
- [5] H.V. Atkinson, S. Davies, Fundamental Aspects of Hot Isostatic Pressing: An Overview, *Metallurgical and Materials Transactions A*, 31A, 2000, 2981- 3000
- [6] B. Ault, “ Matrix Isolation Investigation of the Reaction of $(\text{CH}_3)_3\text{Al}$ with O_2 ,” *Journal of Organometallic Chemistry*, 152, 1999, pp. 169-175
- [7] T. Besshi, T. Sato, T. Tanaka, J. Tamatani, Joining of ceramic green bodies and sintering characteristics, *Journal of Materials Processing Technology*, volume 132, 2003, 269-273

- [8] B.R. Birmingham and H.L. Marcus, "Silicon Carbide Shapes by Selective Area Laser Deposition Vapor Infiltration," *Proceedings of the Solid Freeform Fabrication Symposium* (Austin, TX: Univ. of Texas at Austin, 1994), pp. 348–355.
- [9] B. R. Birmingham, J. V. Tompkins, G. Zong, H. L. Marcus, "Development of a Selective Laser Reaction Sintering Workstation," *Solid Freeform Fabrication Proceedings*, The University of Texas Austin, 147-153, (1992)
- [10] P. Calvert, R. Crockett, "Chemical Solid Free-Form Fabrication: Making Shapes without Molds," *Chem. Mater.* 1997, 9, 650-663
- [11] K-W. Chour, et al, Metal-organic vapor deposition of YSZ electrolyte layers for solid oxide fuel cell applications, *Thin Solid Films*, 304, 1997, 106-112
- [12] P. Colombo, B. Riccardi, A. Donato, G. Scarinci, Joining of SiC/SiCf ceramic matrix composites for fusion reactor blanket applications, *Journal of Nuclear Materials* 278, 2000, pp. 127-135
- [13] J. E. Crocker, H. Wei, L. L. Shaw and H. L. Marcus, "SALDVI of SiC into metal and ceramic powders," *Proceedings of the Solid Freeform Fabrication Symposium*, The University of Texas at Austin (2001), pp. 163–169

- [14] Figueras, S Garelik, J. Santiso, R. Rodroquez- Clemente, B. Armas, C. Combescure, A. Mazel, Y. Kihn, J. Sevely, “ Influence of H₂ Partial Pressure on the Morphology and Crystallization of SiC Layers Obtained by LPCVD Using Tetramethylsilane,” Journal de Physique IV Colloque C2 Supple. Au Journal de Physique II, September 1991 pp C2-225-232.
- [15] Figueras, S Garelik, J. Santiso, R. Rodroquez- Clemente, B. Armas, C. Combescure, R. Berjoan, J. M. Saurel, R. Caplain, “ Groth and Properties of CVD SiC Layers Using Tetramethylsilane,” Materials Science and Engineering, Volume B11, Nos 1-4, January 15, 1992 P83-88
- [16] Figueras, S Garelik, J. Santiso, R. Rodroquez- Clemente, B. Armas, C. Combescure, A. Mazel, M.Ducarroi, W.Zhang, R.Berjoan, “SiCN Coatings Prepared by PACVD from TMS-NH₃-Ar System on Steel,” Journal De Physique IV. 3, 1993, pp. 247-254
- [17] I. M. Ghayad, E. Geiss, J. E. Crocker and H. L. Marcus, “Spot joining of Si₃N₄ and SiC ceramics using selective area laser deposition (SALD) technique,” Proceedings of the Solid Freeform Fabrication Symposium, The University of Texas at Austin (2001), pp. 170–174
- [18] D.N. Goldstein , et al., “Al₂O₃ Atomic Layer Deposition with Trimethylaluminum and Ozone Studied by in Situ Transmission FTIR Spectroscopy and Quadrupole Mass Spectrometry,” Journal of Physical Chemistry. 112, 2008, pp. 19530-19539

- [19] M.D. Groner, et al., "Low-Temperature Al₂O₃ Atomic Layer Deposition," *Chemical Materials*, 16, 2004, pp. 639-645
- [20] S. L. Harrison, "Selective Area Laser Deposition (SALD) Joining of Silicon Carbide with Silicon Carbide Filler," PhD Dissertation, University of Connecticut, 1999
- [21] S.L. Harrison, H. L. Marcus, "Gas-phase Selective Area Laser Deposition SALD/ joining of SiC," *Materials and Design* 20 ,1999. pp 147-152
- [22] Y. Hirose, Y. Terasawa, Synthesis of Diamond Thin Films by Thermal CVD Using Organic Compounds, *Japanese Journal of Applied Physics*, Vol. 25, No. 6, 1986 pp. L519-L521
- [23] IPG Photonics
- [24] K. Jakubenas, H. L. Marcus, "Selective Laser Pyrolysis for Solid Free-Form Fabrication of Silicon Carbide," *Solid Freeform Fabrication Proceedings*, The Univeristy of Texas Austin, 364-370, (1994)
- [25] W. Koh, S.-J. Ku, Y. Kim, Chemical vapor deposition of Al₂O₃ films using highly volatile single sources, *Thin Solid Films* 304,1997, 222-224

- [26] H. Kumagai, et al, Comparative Study of Al₂O₃ Optical crystalline thin films grown by vapor combinations of Al(CH₃)₃/N₂O and Al(CH₃)₃H₂O, Jpn J. Appl. Physics, 32, 1993, 6137-6140
- [27] Leybold Vacuum Products Inc., Vacuum
- [28] W. Lippmann, et al, Laser joining of silicon carbide- a new technology for ultra-high temperature resistant joints, Nuclear Engineering and Design, 231, 2004, 151-161
- [29] M.R. Locatelli, et al., "New Approaches to Joining Ceramics for High-Temperature Applications," Ceramics International. 23, 1997, 313-322
- [30] C. Lue et al, Kinetics of chemical vapor deposition of Sic from methyltrichlorosilane and hydrogen, Applied Surface Science, 255, 2009, 7495-7499
- [31] S. Maleknia J. Brodbelt, "Gas-Phase Selectivities of Crown Ethers for Alkali Metal Ion Complexation," *J. Am. Chem. SOC.* 1992, 114, 4295-4298
- [32] J. Mazumder, A. Kar, Theory and Application of Laser Chemical Vapor Deposition, Springer, 1995
- [33] R.W. Messler, The challenges for joining to keep pace with advancing materials design, Materials and Design, 16#5, 1995, 261-269

- [34] J. Mi, J. Gillespie, R. W. Johnson, S. N. Bondi and W. Jack Lackey, "Silicon carbide growth using laser chemical vapor deposition," Solid Freeform Fabrication Symposium Proceedings Austin, TX, August (2003), pp. 510–523.
- [35] J. Mi, W. J. Lackey, "SiC line deposition using laser CVD," Journal of Materials Processing Technology, Volume 209, Issue 8, 2009, pp 3818-3829
- [36] J.J. Moore, H.J. Feng, Combustion Synthesis of advanced materials
- [37] I. Nasution, et al, Atmospheric pressure chemical vapor deposition mechanism of Al₂O₃ film from AlCl₃ and O₂, Journal of Crystal Growth, 311, 2009, 429-434
- [38] National Instruments, Fundamentals of Motion Control
- [39] S.D. Peteves, "Joining Nitride Ceramics," Ceramics International. 22, 1996, pp. 527-533
- [40] H.O. Pierson, Handbook of Chemical Vapor Deposition, Elsevier, 1999
- [41] D. W. Richerson, Modern Ceramic engineering: Properties, processing, and use in design, New York, Marcel Dekker, 1992

- [42] J. Schroeder et al., Absorbable- Susceptor Joining of Ceramic Surfaces, United States Patent, #4,420,352, 12/1983
- [43] Y.H. Seo, K.S. Nahm, E-K. Suh, H.J. Lee, Y.G. Hwang, Growth mechanisms of 3C-SiC(111) films on Si using tetramethylsilane by rapid thermal chemical vapor deposition, Journal of Vacuum Science and Technology A, Volume 15 Issue 4, 1997, 2226-2234
- [44] Sigma Aldrich
- [45] High Performance Chemicals for Advanced Semiconductor Applications, Sigma Aldrich
- [46] M. Singh, A reaction forming method for joining of silicon carbide-based ceramics, Scripta Materialia, 37(8), 1997, 1151-1154
- [47] M.P. Singh, S. A. Shivashankar, Low-pressure MOCVD of Al₂O₃ films using aluminum acetylacetonate as precursor: nucleation and growth, Surface Coating Technology, 161, 2002, 135-143
- [48] X. Song, C.G. Takoudis, Cyclic chemical- vapor- deposited TiO₂/Al₂O₃ film using trimethyl aluminum, tetrakis(diethylamino)titanium, and O₂, Journal of the Electrochemical Society, 154(8), 2007, G177-G182

- [49] L. Sun, Fundamental studies on selective area laser deposition of graphite, silicon carbide and silicon nitride for in situ device fabrication, PhD Dissertation University of Connecticut, 1999
- [50] H. Tanaka, Sintering of silicon carbide and theory of sintering, Journal of Ceramic Society of Japan, 110(1286), 2002, 877-883
- [51] E.T Thostenson, T. W. Chou, Microwave processing: fundamentals and applications, Composites, Part A 30, 1999, 1055-1071
- [52] A. Varma, A. Rogachev, A. Mukasyan, S. Hwang, Compustion synthesis of advanced materials: Principles and Applications, Advances in Chemical Engineering 24, 1998, 79-226
- [53] L. Wang, F. Aldinger, Joining of advanced ceramics in green state, Materials Letters 54, 2002, 93-97
- [54] C. M. Weiss, H.L. Marcus, "Al₂O₃ Precursor Evaluation for SALD Joining," Proceedings of the Solid Freeform Fabrication Symposium, The University of Texas at Austin (2010)

[55] C. M. Weiss, M. Aindow, H. Marcus, "Ceramic Joining by Gas Phase Pulsed Laser Processing," *Solid Freeform Fabrication Proceedings*, The University of Texas Austin, (2009)

[56] Weiss, C.M., Marcus, H., "Selective Area Laser Deposition for Silicon Nitride Joining," *Solid Freeform Fabrication Proceedings*, The University of Texas Austin, (2012)

[57] G. Zong, R. Carnes, H. G. Wheat, H. L. Marcus, "Solid Freeform Fabrication by Selective Area Laser Deposition," *Solid Freeform Fabrication Proceedings*, The University of Texas Austin, 83-90, (1990)

[58] G. Zong, J.V. Tompkins, W.R. Thissell, E. Sajot, H. L. Marcus, "Processing Problems Associated with Gas Phase Solid Freeform Fabrication Using Pyrolytic Selective Area Laser Deposition," *Solid Freeform Fabrication Proceedings*, The University of Texas Austin, 271, (1991)